

# ANNUAL REVIEW OF PHYSICAL CHEMISTRY

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PREFACE

Physical chemistry has been defined as everything that is of scientific interest to a physical chemist. The twenty-one fields reviewed here represent the committee's best judgment of a practicable compromise in this very broad domain. Sixteen of the chapters in this volume treat the same fields as were treated last year. The chapter on Solutions of Electrolytes is included in this volume and was absent from the last only because the author was unable to complete his review in time last year. As a matter of policy, certain fields are reviewed only occasionally. Thus the four chapters (a) Electrode Processes; (b) Organic Reaction Mechanisms; (c) Physical Chemistry of Proteins; and (d) Bond Energies appearing in this volume replace the following four chapters reviewed last year: (a) Heterogeneous Equilibria and Phase Diagrams; (b) Statistical Mechanics; (c) High Temperature Chemistry; and (d) Isotopes.

There is a considerable variety of opinion among the users of Annual Reviews as to what type of review is most useful. Some would have the author emphasize completeness at all costs. Others want a critical survey within the purview of the particular specialist writing the chapter, even at the cost of completeness. It is the committee's judgment that the present method of securing the best reviewer available each year enables us to cover, over a period of years, all facets of a field better than in any other way.

The committee solicits advice on all aspects of our *Review*. Every effort is now being made and will continue to be made to increase its usefulness. The generous and wholehearted support of both authors and readers is a continuing source of satisfaction, and we express here, again, our deep appreciation.

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# THERMOCHEMISTRY AND THERMODYNAMIC PROPERTIES OF SUBSTANCES<sup>1</sup>

BY EDGAR F. WESTRUM, JR.

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In addition to the growing scientific and technological utilization of free energy and thermal data for the determination of the stability of chemical substances and the position of equilibrium in chemical reactions, the application of thermodynamic methods in the study of the details of structure and of the energetics of atoms, gaseous molecules, crystals, liquids, and the vitreous state is steadily increasing. Limitations of space, however, make it impossible to include in this review all topics of thermodynamic interest. No survey is given of work on the thermodynamics of surfaces, of adsorption phenomena, of bond energies, or of isotopic equilibria; some aspects of solutions, liquid helium, and other items of physicochemical interest have been only partially surveyed. Work in some of these fields is reviewed elsewhere in this volume. Yet even within the narrowed scope of this endeavor, the number of significant recent research publications is so great that even a brief mention would exceed the allotted space for this chapter. Most of these publications are, therefore, concisely represented by entries in tables of chemical thermodynamic studies. Tables I and II list, for inorganic and organic substances, respectively, the nature and source of data recently reported. Letter symbols provide a code of properties, and literature citations refer to the bibliography at the end of the chapter. Studies of chemical equilibria that did not lead to values of the enthalpy or free energy of formation are summarized in Table III; those studies which did lead to definite values of  $\Delta H_f^\circ$  or  $\Delta F_f^\circ$  are included in Tables I and II. These tables will serve to show the considerable range of current thermal and thermochemical investigations and will serve as a basis of discussion, in the text of this chapter, of significant developments and important trends.

*Physical constants and tabulations of data.*—The thermodynamic properties of the elements in their standard states have been tabulated by Stull & Sinke (310). Coughlin (72) has summarized available data on the heats and free energies of formation of the inorganic oxides. Graphs of  $\Delta F_f^\circ$  for oxides to temperatures as high as 2400°C. have been prepared by Tripp & King (326) to facilitate application to ceramic systems. Two compilations of special interest to calorimetrists are the *Thermochemical Bulletin* of Waddington & Skinner (337) and the *Bulletin of Unpublished Thermal Data* of Westrum (341), which list information concerning unpublished studies in their respective fields. A comprehensive tabulation of the thermodynamic properties of organic compounds remains a desideratum.

<sup>1</sup> This review covers recent publications available to the reviewer before January 1, 1957.

The *Tenth General Conference on Weights and Measures* has accepted a redefinition of the Kelvin (absolute) temperature scale in the manner that Kelvin said "must be adopted ultimately" by assigning a value for the temperature of a single fixed point, viz. 273.16°K. for the triple point of water. The ice point, 0.0100°C. below the triple point is, therefore, to be taken as 273.15°K. Definitive papers by Hall (135) and Stimson (302) relate these changes to the International Temperature Scale and, in addition, the latter stresses the need for calorimetrists to use unambiguous heat units. Oishi, Awano & Mochizuki (237) report new determinations of the gold and silver points. An empirical liquid helium vapor pressure equation proposed by Clement, Logan & Gaffney (60) and a thermodynamic calculation of the saturated vapor pressure of helium for use as a temperature scale have been reported (329, 330). Both have been examined by Ambler & Hudson (15), and both represent considerable improvements over the previous "agreed" scale of 1948.

#### STATE DATA AND CHANGES OF STATE

*Transitions.*—Recent advances and new conceptions concerning changes of phase have been presented in a recent volume by Temperley (323). Theoretical papers concerning phase transitions include those of Hill (139), Hurst (151), Ikeda (154), and Jansen & de Wette (158). Especially interesting among the experimental transition studies enumerated in Tables I and II are thorough investigations of the transitions in carbon tetrabromide and ammonium chloride by Marshall, Staveley & Hart (213). In addition to the usual thermal measurements associated with the  $\text{CBr}_4$  transition, these authors also determined the isothermal compressibilities, coefficients of expansion, and densities. From these data the  $C_p$  associated with the transition was found to remain almost equal to  $6R$  showing that the motion of the molecules at the transition does not change to rotation, but remains one of three-dimensional torsional oscillations. For ammonium chloride, while the results are in agreement with the established view of the nature of the  $\lambda$ -point, an "anomalous" contribution to  $C_p$  is evident above the  $\lambda$ -point. Stout & Catalano (54, 55, 304) have made low-temperature thermal measurements on isostructural  $\text{MnF}_2$ ,  $\text{FeF}_2$ ,  $\text{CoF}_2$ ,  $\text{NiF}_2$ , and  $\text{ZnF}_2$ . Using the heat capacity of diamagnetic  $\text{ZnF}_2$  and a corresponding states argument, these authors estimated the lattice contributions to the heat capacity of the remaining compounds (which exhibit heat capacity maxima associated with antiferromagnetic ordering near 70°K.). The magnetic entropies thus calculated are compared with molecular field and spin wave theories of ferromagnetism.

Aston and co-workers (19, 20) have assessed the barrier hindering internal rotation of pentafluorochloroethane as 5300 cal./mole from thermal data and calculations based on spectroscopic data. Aston & Gittler (17) found the barrier in methylammonium chloride to be  $1900 \pm 400$  cal./mole from emf. measurements in anhydrous alcohol, dissociation pressure of the solid, and spectroscopic data. Li & Pitzer (206) have extended tables of

energy levels and thermodynamic functions for internal rotation in molecules with small moments of inertia.

*The vitreous state.*—Otsubo, Haseda & Kanda (240) have shown for vitreous glycerol and isobutanol that the abrupt decrease in the heat capacity at the glass temperature is a function both of the thermal history and of the heating rate during measurements. By utilizing an adiabatic calorimetric technique they were able to show that the decrease was only an apparent one occasioned by the relaxation in the internal configurational change; however, even by this method they were unable to realize the true heat capacity of the glass. Measurements of the heat capacity of glass at high temperatures are reported by Kanai & Akeyoshi (162). Dank & Barber (76) fit the unpublished low-temperature heat capacity measurements of Westrum on vitreous silica with a new function. The quantum theory of heat capacity and the structure of silicate glasses has been discussed by Tarasov (317) and by Myuller (230). Aston, Segall & Fuschillo (18) have made low temperature thermal measurements on a solid solution of 2,2-dimethylbutane (60 mole per cent) and 2,3-dimethylbutane (40 mole per cent). They conclude that the zero-point entropy and heat capacity curves are those of a glass which includes translational freedom in the rotating crystals.

*Gases.*—An additional empirical equation of state for gases designed to provide accurate P-V-T representation from a minimum of data has been proposed by Martin & Hou (215). Bernstein (37, 38) and Spencer (296) discuss the nature and representation of the heat capacity of gases with empirical functions. Free energy functions for the gaseous atoms of atomic numbers to 41 with new or different values for Sc, V, Co, Ga, Zr, and Nb have been calculated by Katz & Margrave (166). Intermolecular potential energy data of dipolar gases may be derived from vapor heat capacity data by methods indicated by Douslin & Waddington (86). Isothermal Joule-Thompson coefficients of some binary gas mixtures have been reported by Charnley *et al.* (56). The basic theory of the volumetric and thermodynamic properties of fluids has been examined by Pitzer *et al.* (251, 252) in relation to the statistical mechanical proof of the theory of corresponding states. Modification of the hypothesis by the addition of one parameter makes it applicable even to slightly polar molecules.

#### HEAT CAPACITY, ENTHALPY, AND ENTROPY

Examination of Tables I and II will indicate that current studies extend throughout the periodic table even including compounds of the synthetic elements and that a large fraction of the studies are in the field of inorganic chemistry. Thorough investigations of systematically selected organic compounds have been contributed by the thermodynamics laboratory of the Bureau of Mines Station at Bartlesville.

*Low temperature thermal measurements.*—Among the major problems currently confronting cryogenic calorimetrists utilizing low temperature data for chemical thermodynamic purposes are those associated with the extrapolation of heat capacities below the lowest temperature at which

measurements are made. Most current definitive studies are carried to temperatures attainable with liquid hydrogen or liquid helium to minimize the possibility of missing anomalies due to phase transitions, electronic or magnetic ordering, anisotropy, or various perturbations. The importance of low temperatures is exemplified by the reported entropy of zinc ferrite: the entropy at 298.16°K. based on heat capacity measurements carried only to temperatures attainable with liquid nitrogen (173) is in error by about four entropy units because of the existence of an antiferromagnetic ordering process near 9°K. (100, 128).

The application of the heat capacity of solids to the problems of physical chemistry has a long history and includes such names as Dulong, Petit, Mendeleev, Einstein, Debye, Nernst, Lindemann, Born, von Karman, and Raman. In recent years interest has centered in the heat capacity of anisotropic lattices. Recent papers selected from nearly a score published by Tarasov (318, 319, 320) treat applications of Tarasov's theory of chain and layer structures to various substances. Chernoplekov (59) has presented a comprehensive review of this subject. Newell (233) and Komatsu (185) have also presented theoretical studies on the problem of lamellar crystals. Experimental tests of these theories are found in the following measurements: on graphite by De Sorbo (81, 82) and by Keesom & Pearlman (168); on molybdenum disulfide by Smith *et al.* (288) and by Westrum & McBride (343); on molybdenum trioxide by Smith *et al.* (288); on cadmium iodide by Dworkin, Sasmor & Van Artsdalen (89) and by Itskevich & Strelkov (156) who also measured  $\text{CdCl}_2$  and  $\text{CdBr}_2$ . An analysis of the vibrational spectrum of graphite and boron nitride has been made by Newell (234). It appears on both experimental and theoretical grounds that the lattice heat capacity of most substances, both isotropic and anisotropic, will approach  $T^3$  behavior at sufficiently low temperatures. Salter (268) has treated the thermodynamics of crystalline solids.

The resolution of thermal properties into a lattice (vibrational) contribution and electronic or transitional contributions is becoming increasingly important. In studies involving magnetic contributions to the thermal properties, a variety of empirical methods have been employed. For example, Osborne, Westrum & Lohr (239) in a relatively favorable circumstance utilized the heat capacity of isostructural diamagnetic  $\text{ThF}_4$  to represent the lattice contribution of the neighboring actinide  $\text{UF}_4$ ; Stephenson & Morrow (301) translated and rotated the curve of heat capacity versus temperature of diamagnetic  $\text{K}_3\text{Co}(\text{CN})_6$  to approximate that of the lattice of  $\text{K}_3\text{Fe}(\text{CN})_6$  in the region of the anomaly attributed to magnetic effects; Stout & Catalano (304) employed a more sophisticated type of approach which might be described as employing the principle of corresponding states between diamagnetic  $\text{ZnF}_2$  and the isostructural antiferromagnetic difluorides. Another approach has been proposed by Hofmann *et al.* (140) in which they fit the lattice heat capacity by combinations of two Debye functions choosing such values as will yield the theoretical entropy increment for complete disordering of spins, i.e.,  $R \ln (2s+1)$ . Although useful re-



sults are obtained, more complete objectivity in the resolution of thermal contributions is desirable.

Another practical problem, that of surface contributions to the measured thermal properties, is occasioned by the difficulty of preparing compact macroscopic crystals of some materials. Measurements on the effect of particle size on the heat capacity of titanium dioxide by Dugdale, Morrison & Patterson (87) are suggestive. More recently Patterson, Morrison & Thompson (246) have measured the heat capacity of small crystallites of NaCl over the range 9 to 21°K. and compared the results with those of Morrison, Patterson & Dugdale (223) on bulk material. Debye theta values at 9°K. approximate 297°, 304°, and 312° for the bulk sodium chloride and for the fine particles of specific surface 38 sq. m./gm. and 59 sq. m./gm., respectively. Patterson (245) has developed a treatment of the frequency spectra of free lattices and particle size effects and concludes that a monatomic lattice shows a low temperature effect associated with the acoustical modes of vibration, but that with a diatomic lattice an effect is also associated with the optical modes and is apparent at higher temperatures. Giaque (109) has discussed practical difficulties in extending measurements of the heat capacity of microscopic particles to very low temperatures.

*Metals and alloys.*—A compilation and an assessment of the present status of data pertinent to the establishment of free-energy diagrams of metallic alloy systems is to be found in *Metallurgical Thermochemistry* (2nd edition) by Kubaschewski & Evans (197) and *Thermochemical Data of Alloys* by Kubaschewski & Caterall (195). Kleppa (177 to 183) has reported extensive calorimetric measurements on the heat of formation and the thermodynamic properties of binary alloys by the dissolution of the alloys and the components in low-melting liquid metals (176). This method shows promise of providing accurate data on the heats of formation of solid alloys. Calorimetric investigations of gold-nickel alloys include low-temperature heat capacity measurements by De Sorbo (80) and high-temperature heat capacity and entropy measurements by Oriani (238). Kubaschewski & Dench (196) studied heats of formation in the titanium-iron and titanium-aluminum systems.

*Statistical calculations.*—The results of many calculations are included in Tables I and II. Woolley (347) has discussed the formulas from which thermodynamic functions may be obtained for simple polyatomic molecules. A comprehensive treatise, *Statistische Thermodynamik*, by Münster (227) covers many topics of physicochemical interest.

*Miscellaneous.*—Turkdogan (327) has correlated the standard entropies of solid and gaseous inorganic compounds; Erdos & Černý (94) have further expounded their method of thermodynamic similarity; and Johnson & Huang (160) discuss the estimation of the heat capacity of organic liquids based on the additivity of heat capacities of functional groups. Nuclear spin contributions to the low temperature thermodynamic properties of iodine, bromine, and chlorine have been calculated by Dodgen & Ragle (83). Erdos (93) treats thermodynamics in a force field. An item of pedagogic interest is

the discussion of the line integral in chemical thermodynamics by Kallo (161).

#### HEATS AND FREE ENERGIES OF REACTION

An interesting method for the determination of the standard free energy change of an equilibrium chemical reaction from a determination of the heat obtained in forming the equilibrium mixture from the reactants ( $Q_1$ ) and from the products ( $Q_2$ ) has been proposed. For a simple equilibrium reaction of the form  $A + B \rightleftharpoons C + D$ , Benzinger (35) has shown that  $\Delta H = Q_1 - Q_2$  and  $\Delta F^\circ = -2RT \ln Q_1/(-Q_2)$ , provided that the reaction has been carried out in sufficiently dilute solution to justify the assumption of constant partial molal heat contents and unit activity coefficients. Although the applicability of this method may be somewhat limited, it may prove a useful supplement to chemical analytical methods in the determination of the equilibrium constant in biological systems. Benzinger & Hems (36) have applied this calorimetric method to the glutaminase reaction and determined the free energy of adenosinetriphosphate hydrolysis.

The thermodynamic stability of the refractory borides with respect to reactions with nitrogen and carbon have been summarized by Brewer & Haraldsen (46).

*Solutions and nonstoichiometric compositions.*—An extensive treatise, *Thermodynamik der Mischphasen*, by Haase (133) summarizes the classical thermodynamics and the statistical mechanics of multicomponent systems. Theoretical papers pertaining to the temperature dependence of the free energy of mixed crystals by Ilchner (155) and on the entropy of mixing by Haase & Rehage (134) are representative of many contributions. Stubblefield, Eick & Eyring (307, 308) have studied the heats of formation of praseodymium and terbium oxides including several of nonstoichiometric composition, while Gattow & Schneider (108) reported heats of formation for the system copper-selenium. Heats of formation have been measured by a differential calorimetric method for some  $\text{RbCl-RbBr}$  and  $\text{NaCl-NaBr}$  solid solutions by Hovi (142). He showed good agreement between the experimental results and theoretical values predicted by means of Wasastjerna's statistical theory. Other systems investigated include: water-hydrogen peroxide and deuterium oxide-deuterium peroxide by Giguère *et al.* (112); isobutene-tertiary butyl alcohol by Taft & Riesz (315); benzene-ethylene dichloride, acetone-chloroform, and acetone-carbon disulfide by Staveley *et al.* (299); isooctane-perfluoroheptane by Mueller & Lewis (225); trichlorobenzene-hexane, triethylamine-mesitylene, and bromobenzene-cyclohexane by Neckel & Kohler (231).

#### NEW APPARATUS AND TECHNIQUES

*Thermal measurements.*—An interesting application of the heat wave method of Samoilov, claimed to be of comparable accuracy to conventional methods for the determination of the heat capacity of metals near  $4^\circ\text{K.}$ , has

been described by Howling, Mendoza & Zimmerman (143). A variation of the mechanical heat switch employed in adiabatic calorimetry in the helium range is described by Webb & Wilks (340). An adiabatic calorimeter of Aven, Craig & Wallace (24) for use below 20°K. is remarkable in that it uses a constant volume helium gas thermometer as the working thermometer. Other techniques for use in the liquid helium range are described by Kouvel (188) and by Rayne (258). Perhaps the most welcome news to weary cryogenic calorimetrists is the automatic adiabatic calorimeter shield control of Zabetakis (350).

A Bunsen-type isothermal ice calorimeter has been described by Leake & Turkdogan (203). Convenience of operation and a 3.4-fold increase in sensitivity over an ice calorimeter has been achieved by Giguère, Morissette & Olmos (111) and by Jessup (159) by using diphenyl ether (m.p. 26.87°C.) as the working substance. A method of mixtures calorimeter utilizing mercury as the calorimetric liquid to minimize vaporization and condensation errors has been described by Plester, Rogers & Ubbelohde (253). The extrapolation of cooling curves in measurements of heat capacity has been discussed by Egan (90). Precision methods for the determination of the heat of fusion are described by Oelsen, Oelsen & Thiel (236); for the heat of vaporization by Golik *et al.* (118). A wire-ribbon method for determining the heat capacities of gases at micron pressures was shown by Vanderkooi & De Vries (328) to give accurate values. A relative-flow method of calorimetry of fluids, whereby two conventional flow calorimeters connected in a series combination determine the ratio of  $C_p$  in one state to that in another, has been presented by Hoxton & Weiss (144). A new approach to the measurement of specific heat of gases, utilizing the variation of temperature with height within a body of gas in convective equilibrium in a gravitational field, and a calorimeter for securing an approximation to convective equilibrium, are described by Collins & Van Wylen (66). Worthington, Marx & Dole (349) describe a new type of adiabatic calorimeter designed especially for measurements on high polymers to 300°C. Gucker & Christens (130) have developed a high pressure calorimeter for heat capacity of aqueous solutions to the critical temperature.

*Thermochemical.*—A compilation of papers edited by Rossini (265) treats many experimental aspects of bomb and reaction calorimetry as well as the more general aspects of modern thermochemistry. Another monograph on reaction calorimetry by Roth & Becker (266) covers both static and dynamic methods of measurement. A notable advance in the procurement of accurate values of the heats of combustion and formation of organic fluorine compounds has been made by Good, Scott & Waddington (119) in the modification and improvement of the design of the rotating-bomb calorimeter. A vacuum-jacketed, precision, combustion calorimeter designed by Aitken, Boxall & Cook (6) minimizes the transfer of heat between the calorimeter bomb and the jacket. An aneroid precision bomb calorimeter for determining heats of combustion has been devised by Pilcher & Sutton (250). Other as-

pects of combustion calorimetry have received attention of Mott and co-workers (28, 224).

Several applications of direct calorimetry to slow reactions have been reported in the current period. A calorimeter used for measurement of the heat of hydration of cellulose is described by Charuel & Traynard (57), one for similar studies on calcium aluminates by Calvert & Longuet (49) and on cements by Alegre & Minerbe (7). An isothermal microcalorimeter for the study of the heat of oxidation and dehydration of coal not far above room temperature has been described by Stott (303). The direct calorimetry of slow processes in furnaces as applied to silicate equilibria, heats of devitrification and dissociation was developed by Kröger & Janetzko (194). The general theory of the Calvet microcalorimeter has been treated by Laville (201). At the other end of the rate spectrum is a discussion of dynamic methods for microcalorimetric determinations of short and variable heat effects by Łaźniewski & Sugier (202). New microcalorimeters for solution processes have been described by Hutchinson & Manchester (152), by Hutchinson & White (153), by Kapustinskiĭ and co-workers (164, 165), and by Mishchenko, Pronina & Sukhotin (222). An adiabatic solution calorimeter stirred by oscillation was developed by Benson & Benson (34).

TABLE I  
THERMODYNAMIC PROPERTIES MEASURED OR CALCULATED  
INORGANIC COMPOUNDS

Compound	Property*	Reference	Compound	Property*	Reference
O <sub>2</sub>	ae	(44)	Bi	a	(256)
H <sub>2</sub>	ade	(137)	Bi <sub>2</sub> Se <sub>3</sub>	ou	(107)
H <sub>2</sub> O <sub>2</sub> , HDO <sub>2</sub> , D <sub>2</sub> O <sub>2</sub>	qrstuv	(110)	C <sub>(graphite)</sub>	alqr	(26, 81, 82, 168, 340)
He <sup>3</sup>	abl	(2, 4, 5, 262)	CO <sub>2</sub>	pqrst	(255)
Xe	p	(220)	CBr <sub>4</sub>	dep	(213)
F, F <sub>2</sub> , F <sub>2</sub> O	qrstuv	(96)	HCN, DCN, TCN	stuv	(45)
Cl, Cl <sub>2</sub> , Cl <sub>2</sub> O	qrstuv	(96)	C <sub>2</sub> N <sub>2</sub>	qrst	(267)
ClF, ClF <sub>3</sub>	qrstuv	(96)	SiO <sub>2</sub>	a	(76)
Br, Br <sub>2</sub> , BrF	qrstuv	(96)	SiC	aln	(212)
BrF <sub>3</sub>	ikqrstuv	(96, 263)	Sn	a	(70, 340)
BrCl	qrstuv	(96)	SnS	iu	(260)
I, I <sub>2</sub> , ICl	qrstuv	(96)	PbN <sub>6</sub>	u	(122, 336)
IF, IF <sub>3</sub> , IF <sub>7</sub>	qrstuv	(96)	PbClF	du	(27)
H <sub>2</sub> S to DTS	qrst	(132)	InBr, InI	hjl	(31, 289)
H <sub>2</sub> SO <sub>4</sub> ·3H <sub>2</sub> O, H <sub>2</sub> SO <sub>4</sub> ·4H <sub>2</sub> O	adegl	(141)	InSb	u	(175)
N <sub>2</sub>	pqrst	(346)	TiF, TiCl, TiBr, TiH	hjl	(30)
N <sub>2</sub> , N <sub>3</sub> <sup>-</sup>	u	(122, 123)	TiF <sub>3</sub>	u	(345)
NH <sup>+</sup>	u	(14)	TiN <sub>3</sub>	u	(122, 336)
HN <sub>3</sub>	u	(122, 336)	Zn	j	(29)
NH <sub>4</sub> <sup>+</sup>	qrstu	(10)	ZnF <sub>2</sub>	alqr	(304)
NH <sub>4</sub> N <sub>3</sub>	u	(122)	ZnS	a	(214)
NF <sub>3</sub>	abdefgiklm	(249)	ZnSO <sub>4</sub>	aln	(333)
NH <sub>4</sub> Cl	dep	(213)	ZnSb, Zn <sub>3</sub> Sb <sub>2</sub>	u	(279)
HNO <sub>3</sub> , DNO <sub>3</sub>	qrst	(241)	Zn <sub>3</sub> P <sub>2</sub>	u	(278)
NO <sub>2</sub> NH <sub>2</sub>	u	(257)	Cd	a	(290)
NH <sub>4</sub> NO <sub>3</sub>	adel	(300)	CdCl <sub>2</sub> , CdBr <sub>2</sub>	a	(156)
PH <sub>3</sub> , PH <sub>4</sub> <sup>+</sup>	qrst	(11)	CdI <sub>2</sub>	alqru	(89, 156)
AsH <sub>3</sub>	abdefghijkl mpqrstu	(16, 281)	CdSO <sub>4</sub> ·H <sub>2</sub> O, CdSO <sub>4</sub> ·8/3 H <sub>2</sub> O	alqr	(242)

\* Key to letter symbols for thermodynamic properties:

- |   |                                |   |  |
|---|--------------------------------|---|--|
| a | $C_p$ or $C_{state}$ of solid  | l | Entropy of solid or liquid                         |
| b | $C_p$ or $C_{state}$ of liquid | m | Entropy of gas                                     |
| c | $C_p$ of gas                   | n | High temperature enthalpy                          |
| d | Transition temperature         | o | Heat of combustion                                 |
| e | Heat of transition             | p | Data of state                                      |
| f | Triple point                   | q | $F^\circ - H_0^\circ$ or $(F^\circ - H_0^\circ)/T$ |
| g | Heat of fusion                 | r | $H^\circ - H_0^\circ$ or $(H^\circ - H_0^\circ)/T$ |
| h | Sublimation pressure of solid  | s | $S^\circ$ or $S^\circ - S_0^\circ$                 |
| i | Vapor pressure of liquid       | t | $C_p^\circ$  |
| j | Heat of sublimation            | u | $\Delta H_f^\circ$                                 |
| k | Heat of vaporization           | v | $\Delta F_f^\circ$                                 |

TABLE I—(continued)

Compound	Property*	Reference	Compound	Property*	Reference
Hg	abgi	(186, 290, 295)	V	a	(69, 348)
Hg <sub>2</sub> N <sub>8</sub>	u	(122, 336)	VO <sup>++</sup> , VO <sub>2</sub> <sup>+</sup>	su <sub>v</sub>	(200)
Cu	a	(68, 258)	V <sub>2</sub> O <sub>5</sub> ·H <sub>2</sub> O	su <sub>v</sub>	(200)
CuN <sub>2</sub> , CuN <sub>8</sub>	u	(122, 336)	VNH <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub>	a	(101)
Ag	a	(68, 167)	NbC	ou	(210)
AgI	e	(33)	Cd <sub>2</sub> Nb <sub>2</sub> O <sub>7</sub>	ade	(77)
AgN <sub>3</sub>	u	(122, 336)	Ta	a	(64, 348)
Au	a	(68)	TaN	ouv	(211)
AuF <sub>3</sub>	u	(345)	Ti	a	(23)
Ir	a	(63)	TiO <sub>2</sub>	a	(87)
Re <sub>2</sub> O <sub>7</sub>	alqr	(48)	TiCl <sub>2</sub>	hjsu	(9, 33, 62, 193, 270)
Rh	a	(63)	TiCl <sub>3</sub>	hisu	(9, 61, 193, 269, 270, 271, 283)
Ni	a	(191, 259)	TiCl <sub>4</sub>	lsu	(9, 97, 129, 193, 270)
NiO	aln <sub>r</sub>	(324)	Zn <sub>2</sub> TiO <sub>4</sub>	aln	(41, 169)
NiF <sub>2</sub>	alqr	(54)	FeTiO <sub>4</sub> , FeTiO <sub>5</sub>	ln	(41)
NiN	ouv	(211)	Zr	qrst	(184)
Ni(CO) <sub>4</sub>	alu	(285, 297, 313)	ZrN	ouv	(211)
CoF <sub>2</sub>	alqr	(55)	ZrC	ou	(210)
Stainless Steel	an	(309)	BO, B <sub>2</sub> O <sub>3</sub> , B <sub>2</sub> O <sub>5</sub>	u	(294)
FeF <sub>2</sub>	alqr	(55)	BH <sup>-</sup> <sub>4</sub> (aq.)	u	(131)
FeS	al	(342)	B <sub>10</sub> H <sub>14</sub>	abghiklqrs	(105)
FeTe <sub>2</sub>	al	(342)	BF <sub>4</sub> <sup>-</sup>	qrst	(13)
Fe(CO) <sub>5</sub>	qrst	(174)	B <sub>4</sub> C	alnou	(212, 287)
FeCo <sub>2</sub> O <sub>4</sub>	al	(173)	Al <sub>2</sub> O <sub>3</sub>	alnqrst	(102, 339)
ZnFe <sub>2</sub> O <sub>4</sub>	aluv	(100, 114, 128, 173)	ZnAlO <sub>2</sub>	uv	(113)
NiFe <sub>2</sub> O <sub>4</sub>	al	(173)	FeAl <sub>2</sub> O <sub>4</sub>	al	(173)
CoFe <sub>2</sub> O <sub>4</sub>	al	(173)	Al <sub>2</sub> TiO <sub>5</sub>	aln	(41, 169)
Fe <sub>3</sub> O <sub>4</sub>	a	(189)	Yb	ou	(146)
α- and β-Mn	a	(43)	YbCl <sub>3</sub>	u	(209)
MnCl <sub>2</sub>	a	(187, 229)	Er	alqr	(147, 284)
MnBr <sub>2</sub> ·4H <sub>2</sub> O	al	(163)	Dy	adeglorsu	(127, 146)
Cr	a	(259)	Tb <sub>2</sub> O <sub>3</sub>	u	(308)
CrI <sub>2</sub>	hj	(8)	Gd	u	(148)
Cr(CO) <sub>6</sub>	u	(71)	Sm	u	(150)
MoO <sub>3</sub>	u	(298)	SmCl <sub>3</sub>	u	(209)
MoO <sub>4</sub>	alqr	(288, 298)	Am	ik	(51)
MoO <sup>-4</sup> (aq.)	uv	(120)	AmF <sub>3</sub>	hj	(50)
H <sub>2</sub> MoO <sub>4</sub>	u	(120)	PuF <sub>3</sub>	hj	(50)
MoS <sub>2</sub>	alqr	(288, 343)	UO <sub>3</sub>	hj	(3)
Mo(CO) <sub>6</sub>	alru	(22, 71)	UH <sub>3</sub> , UD <sub>3</sub> , UT <sub>3</sub>	u	(1)
MoSi <sub>2</sub>	an	(339)	UF <sub>4</sub>	alqr	(239)
Ag <sub>2</sub> MoO <sub>4</sub>	u	(226)			
W	a	(338)			
W(CO) <sub>6</sub>	u	(71)			

TABLE II—(continued)

Compound	Property*	Reference	Compound	Property*	Reference
UI <sub>3</sub>	al	(261)	NaH	u	(219)
UO <sub>2</sub> Cl <sub>2</sub>	alqr	(124)	NaCl	a	(214, 223, 246)
UOCl <sub>2</sub> , UOBr <sub>2</sub>	alqr	(125)	NaN <sub>3</sub>	u	(122)
Be	alqr	(138)	NaNO <sub>3</sub>	abglqr	(292)
Mg	an	(309)	Na <sub>2</sub> SO <sub>4</sub>	abegn	(73)
MgCd <sub>2</sub>	ae	(264)	NaFeO <sub>2</sub>	al	(171)
MgO·Al <sub>2</sub> O <sub>3</sub>	aln	(42, 172)	Na <sub>2</sub> MoO <sub>4</sub>	u	(120)
Ca	u	(149)	NaBO <sub>2</sub>	alqr	(126)
CaN <sub>6</sub>	u	(122)	NaBH <sub>4</sub>	u	(12)
Ca(PO <sub>3</sub> ) <sub>2</sub>	abglqr	(91)	NaAlO <sub>2</sub>	al	(171)
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	alu	(92)	NaAlSi <sub>2</sub> O <sub>6</sub> ·H <sub>2</sub> O	al	(170)
Ca <sub>2</sub> SiO <sub>4</sub> ·H <sub>2</sub> O	u	(235)	K, K <sub>2</sub>	aqrstuv	(78, 95)
Ca <sub>3</sub> Si <sub>3</sub> O <sub>11</sub> ·3H <sub>2</sub> O	u	(235)	KO <sub>2</sub>	u	(116)
Ca <sub>3</sub> Si <sub>3</sub> O <sub>18</sub> ·H <sub>2</sub> O	u	(235)	KH	u	(219)
CaO·Al <sub>2</sub> O <sub>3</sub>	alnu	(42, 74, 172)	KCl	a	(340)
CaO·2Al <sub>2</sub> O <sub>3</sub>	aln	(42, 172)	KN <sub>3</sub>	u	(122)
12CaO·7Al <sub>2</sub> O <sub>3</sub>	alnu	(42, 74, 172)	KNO <sub>3</sub>	adg	(291, 293)
3CaO·Al <sub>2</sub> O <sub>3</sub>	aln	(42, 172)	KSCN	g	(253)
Ca <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	al	(169)	KBH <sub>4</sub>	u	(12)
SrN <sub>8</sub>	u	(122)	KCl·ZnSO <sub>4</sub>	aln	(333)
BaN <sub>6</sub>	u	(122)	KBr·ZnSO <sub>4</sub>	aln	(333)
Li	ablnqr	(84)	Li <sub>2</sub> SO <sub>4</sub> ·K <sub>2</sub> SO <sub>4</sub>	abdegl	(332)
Li, Li <sub>2</sub>	qrstuv	(95)	K <sub>3</sub> Co(CN) <sub>6</sub>	aelgruv	(301)
Li <sub>2</sub> O	aln	(282)	K <sub>4</sub> Fe(CN) <sub>6</sub>	algruv	(301)
LiH	u	(219)	K <sub>2</sub> CrO <sub>4</sub> , K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	al	(254)
LiOH	abgl	(282)	Rb, Rb <sub>2</sub>	qrstuv	(78, 95)
LiF	abgl	(214, 335)	RbN <sub>3</sub>	u	(122)
Li <sub>2</sub> SO <sub>4</sub>	abdegl	(331)	RbBH <sub>4</sub>	u	(12)
LiN <sub>3</sub>	u	(122)	RbCl·ZnSO <sub>4</sub>	u	(334)
Li <sub>3</sub> Sb	u	(280)	Cs	agqrstuv	(65, 78, 95)
LiFeO <sub>2</sub> , LiAlO <sub>2</sub>	al	(171)	Cs <sub>2</sub>	qrstuv	(95)
Li <sub>2</sub> TiO <sub>3</sub>	al	(169)	CsN <sub>3</sub>	u	(122)
Na, Na <sub>2</sub>	aqrstuv	(95, 243)	CsCl·ZnSO <sub>4</sub>	u	(334)
NaO <sub>2</sub> , Na <sub>2</sub> O <sub>2</sub>	u	(116)	CsBH <sub>4</sub>	u	(12)

TABLE II  
THERMODYNAMIC PROPERTIES MEASURED OR CALCULATED  
ORGANIC COMPOUNDS

Compound	Property*	Reference
Ethylene	prs	(75)
Heptane	abcfqlnqrst	(85)
(2,2-Dimethylbutane) <sub>2</sub> (2,3-dimethylbutane) <sub>1</sub>	abegl	(18)
2,3-Dimethyl-2-butene	abdefgklqrst	(273)
Cycloheptane, cyclooctane	abefgiklmpqrurv	(99)
1,2,3-Trimethylbenzene	abdefglm	(321)
1,2,4-, and 1,3,5-Trimethylbenzenes	b	(136)
1,3,5-Trimethylbenzene	aglm	(322)
Diphenylene	io	(52)
Biphenyl	cm	(325)
Azulene, guaiazulene	ou	(190)
Polyisobutylene	abelqrst	(106)
1,3,5-Cycloheptatriene	abdefgiklmpqrurv	(99)
Twenty-two alkylnaphthalenes	qrst	(221)
Methanol	qrst	(157)
1-Heptanol	abgluv	(244)
Cyclopentanol	abgluv	(244)
1,2,3,4-Tetrahydronaphthalene	qrst	(314)
Hexadecanol	aluv	(244)
<i>n</i> -Butyraldehyde	abgluv	(244)
Paraldehyde	o	(53)
<i>n</i> -Heptaldehyde	abgluv	(244)
Polycaprolactam	a	(217)
Furfuryl alcohol	abluv	(244)
Furan	st	(25)
Glycidol	o	(40)
Dimethyl ether	qrst	(277)
Methyl ethyl ketone	abgluv	(244)
Succinic acid	ou	(250)
Benzoic acid	o	(67)
Palmitic acid	alqrs	(344)
<i>d</i> -Camphor, <i>dl</i> -camphor	aln	(272)
Methyl palmitate	alqrs	(344)
Polyethylene terephthalate	abf	(286)
Methyl amine	ls	(17)
Trimethylhydrazine	abgils	(21)
Ethyl nitrate	iku	(121)
CF <sub>4</sub> , C <sub>2</sub> F <sub>4</sub> , C <sub>3</sub> F <sub>6</sub> , (C <sub>2</sub> F <sub>4</sub> ) <sub>2</sub> , (C <sub>2</sub> F <sub>4</sub> ) <sub>n</sub>	u	(88)
Tetrafluoromethane, tetrafluoroethylene	u	(232, 274)
Polytetrafluoroethylene	alou	(119, 216, 274)
Butadiene-styrene copolymers	a	(103)

\* Code for letter symbols is identical with that of Table I.



TABLE II—(continued)

Compound	Property*	Reference
Fluorobenzene	abcfgiklmpqrstuv	(119, 276)
Benzotrifluoride; <i>o</i> -, <i>m</i> -, and <i>p</i> -fluorobenzoic acids	u	(119)
CHF <sub>3</sub> , CClF <sub>3</sub> , CH <sub>3</sub> CF <sub>3</sub>	c	(328)
CH <sub>3</sub> CF <sub>3</sub> , CHFCHF	ou	(232)
C <sub>2</sub> F <sub>4</sub> Cl	abegikl	(19)
CH <sub>3</sub> Cl, C <sub>2</sub> H <sub>5</sub> Cl	u	(199)
C <sub>2</sub> H <sub>5</sub> Cl	bpu	(115, 199)
CHCl <sub>2</sub> CHCl <sub>2</sub>	abgklmqrst	(205)
1,2,3-Trichloropropane, propyl chloroacetate, amyl chloride, butyl chloroacetate, <i>p</i> -chlorobenzoic acid, and <i>o</i> -dichlorobenzene	o	(40)
CBr <sub>4</sub>	adep	(213)
1-Propanethiol	abcdefgkmpqrstuv	(248)
1-Pentanethiol, 3-thiapentane	u	(312)
3-Methyl-2-thiabutane	abgklmpqrstuv	(218)
5-Thianonane	ou	(312)
Thiophene	oqrsuv	(145, 311)
2-Methylthiophene	abcfklmpqrstuv	(247)
Methylisothiocyanate	ou	(312)
Thioacetic acid	ou	(311)
Trimethylsulfonylmethane	al	(79)
B(CH <sub>3</sub> ) <sub>3</sub> BF <sub>3</sub>	an	(32)
(CH <sub>3</sub> ) <sub>2</sub> NB <sub>2</sub> H <sub>3</sub>	abefgiklqrt	(104)
Epichlorohydrin, chloropropanediols, and dichloropropanols	o	(40)
(CH <sub>3</sub> O) <sub>3</sub> P, (C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> P	u	(58)
Sodium acetate	adl	(305)
Lead oxalate	u	(275)
Sodium succinate	al	(306)
Ru(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> , Ni(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> , and Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	qrst	(207)
Twelve organosilicon compounds	o	(117)
Sb(CH <sub>3</sub> ) <sub>3</sub>	u	(208)
Cd(CH <sub>3</sub> ) <sub>2</sub>	abdeiklm	(204)
Pb(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>	ou	(275)
B(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	u	(316)
Copper phthalocyanine	e	(39)

TABLE III

CHEMICAL EQUILIBRIA STUDIED

Equation	Reference
$\text{CF}_3\text{CF}_2 + \text{Br}_2 = \text{CBrF}_2\text{CBrF}_2$ , etc.	(198)
$\text{CH}_3\text{Cl} + \text{H}_2 = \text{CH}_4 + \text{HCl}$ , etc.	(199)
$\text{CH}_2\text{CH}_2 + \text{HCl} = \text{C}_2\text{H}_5\text{Cl}$	(199)
$\text{CH}_3\text{CHCl} + \text{H}_2 = \text{C}_2\text{H}_5\text{Cl}$	(199)
$\text{C}_2\text{N}_2 = 2\text{CN}$	(267)
$3\text{TiCl}_2 = 2\text{TiCl}_3 + \text{Ti}$	(98)
$2\text{TiCl}_2 = \text{TiCl}_4 + \text{Ti}$	(98)
$3\text{TiCl}_4 + \text{TiC} = 4\text{TiCl}_3 + \text{C}$	(283)
$2\text{TiCl}_3 = \text{TiCl}_2 + \text{TiCl}_4$	(270, 283)
$\text{TiCl}_3 + \text{HCl} = \text{TiCl}_4 + \frac{1}{2}\text{H}_2$	(192)
$\text{TiCl}_4 + 2\text{H}_2 + \frac{1}{2}\text{N}_2 = \text{TiN} + 4\text{HCl}$	(228)
$2\text{UO}_2 = \text{U}_2\text{O}_4$	(3)
$\text{Ca}_2\text{SiO}_4 = \beta\text{-Ca}_2\text{SiO}_4 + \text{CaO}$	(47)
$2\text{NaCl} + \text{Ti} = 2\text{Na} + \text{TiCl}_2$	(283)

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# CRYOGENICS<sup>1</sup>

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## INTRODUCTION

This vigorous field of science has spread itself across chemistry and physics such that international conferences lasting four days are held every two years and the journals bulge with original articles. There have been monographs (1), review articles (2), annual progress reports (3), and books written at the popular (4) and graduate student (5) level. An annual bibliography for the field of cryogenics (6) has done much towards keeping scientists informed. With all this available to anyone anxious to cover "everything," we have rather taken as our task in this brief article a simple survey of what seems to us most interesting in the current research efforts in cryogenics. The specialist in cryogenics will have already read the original articles or heard a presentation at some science meeting so this review is not for him. What seems too highly controversial (or just not understood!) has been omitted and can be discussed by another writer another year.

## THE PRODUCTION AND MEASUREMENT OF LOW TEMPERATURES

The helium liquefiers developed recently have been described by Collins (7) in a review article and this serves as an excellent introduction to his latest machine (8) of 45 l. per hour capacity which is driven by a 90-hp. compressor and uses 25 l. of liquid nitrogen per hour. Such quantities may be used in liquid helium bubble chambers. The group (9) at Oxford University has recently described their new Linde type liquefier for more modest needs which produces one liter per hour. The sharp contrast in the requirements of different research groups is thus clearly brought out by these two capacity figures. That size has nothing to do with excellence is clearly demonstrated by the appearance from Oxford University of the most exciting experimental work in cryogenics during 1956—the nuclear cooling of copper to the amazingly low temperature of  $2 \times 10^{-8}$  °K. The work was done by the late Sir Francis Simon and his co-workers, Kurti, Robinson & Spohr (10). These experiments have shown that by using nuclear demagnetization, one can reach temperatures below those accessible with electron paramagnetics. New scientific horizons have been opened for studies of nuclear spins in solids. The concept of temperatures near absolute zero has been reviewed by Sir Francis Simon (11), and it is just the spin system temperature itself which brings him to urge that we give up the popular idea of thinking of temperature in terms of disordered kinetic energy. This is particularly true of nuclear spin systems where "negative temperatures" may be said to exist (12). For this, experi-

<sup>1</sup> The survey of literature pertaining to this review was concluded in December, 1956.

mental conditions may be so arranged that there is a distribution of nuclear particles over available energy states which is hotter than infinite (13). This is clearly not cryogenics! The techniques of magnetic thermometry have been reviewed by van Dijk (14), and in the same volume one may find valuable information about gas thermometry and vapor pressure temperature scales in the region of interest to the cryogenist. Keller (15) has discussed the effort towards international agreement on a temperature scale between  $1^{\circ}$  and  $5.2^{\circ}\text{K}$ . using the vapor-pressure of liquid helium. He believes that the scale offered by Clement (16), called  $T_{\text{SE}}$ , more closely represents actual vapor-pressure measurements as determined in the laboratory. The scale proposed by van Dijk & Durieux (17) from the Kamerlingh-Onnes Laboratory at Leiden University, called  $T_{\text{LS}}$ , may be obtained from the director of that laboratory in the form of tables (March, 1956). The two scales differ by at most  $0.0036^{\circ}\text{K}$ . below  $4.2^{\circ}\text{K}$ . and the difference is more serious above this temperature. The National Bureau of Standards has taken a vigorous part in this problem. Ambler & Hudson (18) measured the variation of the mutual inductance of two coils surrounding a paramagnetic crystal (a sphere of chromic methyl-ammonium alum) as a function of the saturation vapor-pressure of helium in the range  $1.3^{\circ}$  to  $4.2^{\circ}\text{K}$ . and find close accord with the thermodynamic calculation of van Dijk & Durieux, but even closer with  $T_{\text{SE}}$ . Tables of  $T_{\text{SE}}$  are available from the Naval Research Laboratory, Washington, D.C. These matters were fully discussed in the cryogenics article by Berman, Cooke, and Hill in Volume 7 of this series, and our comments are meant to bring matters up-to-date.

#### SUPERFLUIDS

*Liquid helium.*—As is well known, there are the two isotopes of helium,  $\text{He}^3$  and  $\text{He}^4$ , and then we speak (but clearly write) of  $\text{He}^4$  as having liquid forms I and II. Both isotopes form liquids which manifest quantum characteristics. It is certainly an error to think of the superfluid liquid II of  $\text{He}^4$  as being the only nonclassical one of the family. The liquid form of  $\text{He}^3$  has disclosed some interesting results in the hands of those fortunate enough to get an ample supply of the rare isotope (19). These scientists have measured the thermodynamic properties of liquid  $\text{He}^3$  down to  $0.2^{\circ}\text{K}$ . The entropy vs. temperature is not linear (Fermi-Dirac gas), and at  $0.5^{\circ}\text{K}$ . the entropy has, indeed, dropped below a linear extrapolation of the higher temperature results. Thus, the specific heat has an almost flat region between  $0.2^{\circ}$  and  $0.6^{\circ}\text{K}$ . with a large value of  $\sim 0.8$  cal./deg.-mole. Fairbank *et al.* (20) showed that the nuclear spin magnetic susceptibility deviated from a  $1/T$  dependence just in this temperature region and in such a way that antiparallel alignment between nuclei was being manifest. The temperature at which the susceptibility has fallen to 80 per cent of the Curie value is about  $0.45^{\circ}\text{K}$ . for  $\text{He}^3$  under its saturated vapor. Under a pressure of 22 atm. (not yet solid), the spin interaction is decreased and one (21) must go down to  $0.33^{\circ}\text{K}$ . for the same 80 per cent of the Curie value. We understand that in the solid

phase such spin interaction does not occur until  $\sim 10^{-6}$  °K. One knows that in the electronic paramagnetic substance deviations from Curie's law may occur because of coupling and of "exchange effects." These exchange effects exist if electronic wave functions overlap. We must conclude that below 1°K. this is so for the liquid He<sup>3</sup> in that nuclear wave functions overlap. Houston & Rorschach (22) regard the wave function overlap to lead to a motion of the nuclei through a periodic potential field—much like the Bloch treatment of electrons in a metal. They calculate a magnetic susceptibility for the nuclei which strongly resembles the observed values. There have been several other theoretical approaches (23 to 26). These men have all been concerned over the very high entropy value still present in liquid He<sup>3</sup> below 1°K. and have, therefore, looked for modes of energy excitation which are in addition to the energy of elastic waves. They have generalized the Lennard-Jones cell method of treating the liquid state to include cell clusters of two or more cells commonly shared by two or more molecules. In this way exchange effects are introduced and, in particular, the consideration of the motion of two helium atoms in a double cell gives a set of excited states to be identified with the quantum mechanical treatment of the rigid rotator. The symmetry requirements, i.e., the statistics to be used, now require the eigen states of He<sup>3</sup> to have the extra statistical weights 1, 3, 1, etc. (just as for H<sub>2</sub>) because of nuclear magnetic spin moment. Furthermore, the first excited state of rotational quantum number  $J=1$  lies quite low for He<sup>3</sup> and gives rise to most of the entropy observed in the liquid at 1°K. The same cell model applies to He<sup>4</sup> liquid but the eigen states are limited to  $J=0, 2, 4$  for double-cell occupancy (no nuclear moment). However, here the excited rotational state is much higher so that contribution to the entropy comes only well above 1°K. There is the problem of connecting these ideas up with the superfluid behavior of He<sup>4</sup> and we may hope for more work on the theory of liquid helium by these authors. Feynman *et al.* (27) have continued the problem of describing the excitations in liquid helium II of the isotope He<sup>4</sup>. They agree with Landau (28) that the excitations consist of (a) quantized sound waves, and (b) some kind of rotation of the fluid, "rotons," which is pictured now as the quantum-mechanical analogue of a smoke ring, i.e., a microscopic vortex ring of diameter about equal to the atomic spacing. A forward motion of single atoms through the center of the ring is accompanied by a dipole distribution of returning flow far from the ring. All this new work on the excitations does not imply that the basic idea of London (29) of a Bose-Einstein condensation as the "reason" for the lambda-transition in liquid He<sup>4</sup> has been set aside. Penrose & Onsager (30) promise to bring these matters into sharper focus. These authors discuss the work of Bogolyubov *et al.* (31) for nonideal Bose-Einstein gas and they present arguments based on first principles for the condensation concept of London. They say roughly 8 per cent of the atoms are "condensed." Mikura (32) uses an energy gap in the Bose-Einstein theory for liquid helium.

The basic experimental facts of superfluid liquid He<sup>4</sup> are far in advance



of the theoretical understanding and very little startlingly new experimental evidence has been brought out recently. Bots & Gorter (33) have measured the fountain effect down to  $0.1^\circ\text{K.}$  with the aid of magnetic cooling. Below  $0.75^\circ\text{K.}$ , experiment does not agree closely with present theory. The slow neutron diffraction studies on liquid  $\text{He}^4$  by Hurst & Henshaw (34) indicate that at low temperature the average atom in liquid helium has approximately eight first neighbors at a mean distance of 3.7 Å and perhaps eleven neighbors at a distance of 5.25 Å. The observed width of the diffraction peak would require that the order in lattice type structures is not rigidly preserved beyond a range of a few atomic spacings. Hurst & Henshaw observed little change, if any, in the scattering distribution (and corresponding density distribution) on crossing the lambda point temperature. Nevertheless, they speculate that the small changes which take place in the radial distribution function may be sufficient to produce nonlocalized "running levels" associated with superfluidity. No comments are made on this by Mazo & Kirkwood (35) in discussing the radial distribution function for liquid helium. Goldstein & Sommers (36) give the slow neutron total scattering cross section in liquid  $\text{He}^4$  and in the discussion emphasize the large zero-point kinetic energy. We conclude this survey of experiments on liquid helium with mention of the studies by Holm & Herlin (37) on the viscosity, by Osborne (38) on heat flow below  $0.6^\circ\text{K.}$ , and by Fairbank & Wilks (39) on heat transfer below  $1^\circ\text{K.}$  Peshkov (40) has evidence that the second-order transition at the lambda point can become a first-order one by the presence of flowing heat. Finally, the work by Fairbank *et al.* (41) indicates that the specific heat of liquid  $\text{He}^4$  goes very high just at the lambda point.

#### SUPERCONDUCTIVITY

*Recent studies on superconductivity.*—The Westinghouse Research Laboratories have contributed some splendid new experimental results to the understanding of superconductivity. Corak *et al.* (42) were able to show that below  $0.7 T_c$ , where  $T_c$  is the transition temperature, the electronic contribution to the atomic heat,  $C_{es}$  of the metal in the superconducting state could be represented by an exponential expression of the form:

$$C_{es}/\gamma T_c = ae^{-bT_c/T}$$

For vanadium they give the following constants:  $T_c = 5.03^\circ\text{K.}$ ,  $\gamma = (9.26 \pm 0.03) \times 10^{-3}$  joule mole $^{-1}$  deg. $^{-2}$ ,  $a = 9.17$ ,  $b = 1.50$ , and the Debye  $\theta = 338 \pm 5^\circ\text{K.}$  For the studies on pure tin they give (43) the same exponential law below  $0.7 T_c$  and the following constants:

$$\begin{aligned} T_c &= 3.722^\circ\text{K.}, & \gamma &= 1.75 \times 10^{-3} \text{ joule mole}^{-1} \text{ deg.}^{-2}, \\ a &= 9.17, & b &= 1.50, \text{ and } \theta_D = 195.0^\circ\text{K.} \end{aligned}$$

Until recently the available experimental evidence suggested a  $T^3$  dependence for  $C_{es}$ . This was thermodynamically consistent with the parabolic temperature dependence found for the critical magnetic field,  $H_c$ . These features were



incorporated in the Gorter-Casimir (44) two fluid model for superconductors. The two fluid model uses the concept of an energy gap between the super and normal state of the electrons. Slater (45) sought such an energy gap from the band theory of metals although he was never convinced he had proved the necessary perturbation. Slater *et al.* (46) experimentally explored a superconductor for such an energy gap thinking it would cause large absorption of microwaves (3-cm. length in vacuum). Theoretical work (47 to 50) continued to predict such an energy gap. Finally, Blevins, Gordy & Fairbank (51) produced millimeter length electromagnetic waves and found that for Sn, at a frequency such that  $\nu \approx kT_c/h$ , the energy was absorbed even though the temperature was  $T < T_c$ . Similar absorption was found in Al by Biondi, Garfunkel & McCoubrey (52). Their results gave an energy gap at  $T < T_c$  to be greater than  $2.33 kT_c$ . In addition, the decrease in the effective transition temperature with increasing photon energy,  $h\nu$ , would indicate that the gap is not fixed but decreases as  $T \rightarrow T_c$ . So an energy gap seems very real and yet the experiments on the electronic contribution to the atomic heat,  $C_{es}$ , had given rise to doubts of the two fluid model. Two theoretical papers have appeared to throw light on these matters: Lewis (53) has expressed the free energy,  $F$ , per unit volume as a function of  $T$  and of an order parameter  $\omega$ :

$$F = -A\omega - 1/2K(\omega)\gamma T^2$$

where  $A$  is a constant equal to  $H_0^2/8\pi$ ,  $\gamma$  is the electronic specific heat parameter, and  $K(\omega)$  is an arbitrary function [equal to  $(1-\omega)^{1/2}$  in the Gorter-Casimir (44) model]. In the above,  $H_0$  is the critical field at absolute zero of temperature. The parameter  $\omega$  goes from 0 at  $T_c$  to a value 1 at 0°K. The exponential specific heat in a superconductor leads to an expression for  $K(\omega)$ . The effect of this is to make the value of  $\omega$  approach unity more rapidly at  $T \rightarrow 0^\circ\text{K.}$  and also  $H_c$  goes to  $H_0$  more rapidly than in the former Gorter-Casimir (44) model. Chester (54) cautions against separating the electronic term in the way the Westinghouse groups (42) have done.

A group of widely scattered scientists (55 to 58) have contributed to further understanding of a complicated effect known as "Apparent Paramagnetism at the Superconducting Transition." The effect was discovered by Steiner (59) and concerns some extra flux within a superconductor just at the transition and under special conditions.

Buck (60) has developed a superconducting device which he calls *The Cryotron*. In its simplest form, the cryotron consists of a straight piece of wire (in the superconducting state) with a single-layer winding of wire over it. Current in the winding creates a magnetic field which causes the central wire to change from its superconducting state to its normal state (destruction of Meissner Effect with critical field). The device, as a circuit element, has current gain, that is, a small current can control a larger current. It has power gain and can be used as a computer component.

The studies of Schawlow (61) have been most interesting because they

allow one to see and to photograph the magnetic domain pattern of the normal and superconducting regions of the "intermediate state." The method can be used for quantitative measurements of the so-called surface energy between domains. These studies may well prove a major "break through" in the decisions of theories which take into account electronic wave function localization. We will now discuss some of these recent theories.

*Theoretical ideas of superconductivity.*—Superconductivity has now been explored so thoroughly that one is even surprised at the new theoretical ideas brought forth—so many have been tried. At the Proceedings of the Lorentz-Kamerlingh Onnes Memorial Conference (62), Leiden University, June, 1953, the best minds interested in superconductivity discussed the current theories. The Bardeen-Frohlich (63, 64) theory involving the interaction between the electrons through their coupling with the ion lattice was discussed by Professor N. Bohr (62, p. 762). Bohr argues that we have to do in the superconducting phase with a state of the electrons which, although differing very little in energy from the normal one, exhibits a high degree of order, which abolishes all statistical features of free or coupled electron motions and rather corresponds to a wave function in configuration space, adjusted to the interaction between the electrons and the ion lattice, including the impurities, as well as to the mutual interactions between the individual electrons. Recently Haken (65) has approached this problem from a fresh view point. Also, during the past two years Schafroth & Blatt (66), and these authors with Butler (67), have started a program which may eventually satisfy the requirements stated by Professor Bohr. First, they have reasons for modifying the London phenomenological equation for a superconductor. Some of the consequences of having a finite correlation length are: (a) a magnetic field is not completely expelled from a superconductor; the field at a large depth,  $x$ , is proportional to  $x^{-1}$ , rather than dropping off exponentially (see our discussion below for the exponential law). (b) The Pippard (68) effect follows as a natural consequence from the equations proposed by Blatt & Schafroth. Since these new efforts represent the start of a new program, and in one case (68) "a somewhat vague empirical concept," we will now turn to other theories.

Ginzburg & Landau (69), and more recently Ginzburg (70), have developed a macroscopic theory of superconductivity. In weak magnetic fields their theory becomes identical with the London (71) theory but in strong fields they find an important difference. In the London theory an empirical relation is given which correlates an external magnetic field,  $H$ , with the current density of superconducting electrons,  $J_s$ :

$$\text{curl } \Lambda J_s = -H/c$$

The quantity  $\Lambda = m/ne^2$  combines the mass,  $m$ , the charge,  $e$ , and the number of superconducting electrons,  $n$ . The quantity,  $c$ , is for the gaussian units which are still used by old die-hards. This equation defines the property of a superconductor and may be combined with the Maxwell equation (cf. 71) to

give a differential equation for the magnetic field:

$$\nabla^2 H - 1/\delta_0^2 H = 0$$

where  $\delta_0 = (\hbar c^2/4\pi)^{1/2}$  is a penetration depth. The solution for an infinite plane boundary located at  $x=0$  between empty space containing the field  $H_0$  and the superconductor is given by:

$$H = H_0 e^{-x/\delta_0}$$

Thus, the magnetic field does not penetrate much beyond the distance  $\delta_0$  and this is of the order  $10^{-6}$  cm. In strong fields approaching the critical,  $H_c$ , Ginzburg (70) seeks another  $\delta_0$ . The number of superconducting electrons, or rather  $(n)^{1/2}$ , is taken by Ginzburg & Landau as a parameter that measures the second order phase transition, i.e., it is zero for temperatures above the superconducting transition temperature,  $T_c$ . The effective wave function  $\psi$  is introduced such that  $|\psi|^2 = n$ . The density matrix of electrons in the metal is given by the true wave functions of the electrons:

$$\rho(r, r') = \int \psi^*(r, r_i'') \psi(r, r_i'') dr_i''$$

$r_i''$  are the coordinates of all electrons except the one under consideration and for the latter the coordinates are  $r$ . The coordinate  $r'$  is at a second point. Now Ginzburg & Landau use the wave function in an expression for the free energy of a superconductor per unit volume and in a field,  $H$ , of vector potential,  $A$ :

$$F_{SH} = F_{SO} + H^2/8\pi + 1/2m |\psi|^2 (-i\hbar\nabla - e/cA)^2 \psi$$

The value of the free energy density in zero field,  $F_{SO}$ , is given by the approximation (valid at  $T$  near  $T_c$ ):

$$F_{SO} = F_{NO} + \alpha |\psi|^2 + \beta/2 |\psi|^4$$

where  $F_{NO}$  is the free energy density in the normal state, and the energy quantities  $\alpha, \beta$  are to be determined. The minimum in the free energy allows one to vary with respect to  $\psi^*$  (and  $A$ ) so that the following equations define  $\psi$  and  $A$ :

$$\begin{aligned} 1/2m(-i\hbar\nabla - e/cA)^2 \psi + \frac{\partial F_{SO}}{\partial \psi^*} = \\ \nabla^2 A = -\frac{4\pi J_s}{c} = \frac{2\pi i\hbar}{mc} (\psi^* \nabla \psi - \psi \nabla \psi^*) + \frac{4\pi e^2}{mc^2} |\psi|^2 A. \end{aligned}$$

This last equation is found in all textbooks on quantum mechanics (72). For weak magnetic fields we may repeat London's observation that  $|\psi|^2 = n$  and we have the well-known London (71) equation:

$$\nabla^2 A = -\frac{4\pi J_s}{c} = \frac{4\pi e^2}{mc^2} |\psi|^2 A = \frac{4\pi e^2 n}{mc^2} A$$

or

$$\Delta J_s = -A/c \text{ (note that } H = \text{curl } A).$$

But in strong fields this is not so and approximation methods must be used to find the dependence of  $\psi$  on coordinates and magnetic field strength. Certainly in normal diamagnetics the wave function is perturbed by an applied magnetic field. On the surface of the superconductor, where  $\vec{k}$  is the outward normal unit vector:

$$\vec{k}[-i\hbar\nabla\psi - e/cA\psi] = 0.$$

If now  $H=0$  so that  $A=0$  then on the surface  $\nabla\psi=0$  and hence  $\partial F_{SO}/\partial\psi^* = 0$ . For this to be a minimum solution, Ginzburg (73) writes:  $|\psi|^2 = -(\alpha/\beta)$  which is the above electron concentration,  $n$ , at  $H=0$ . With temperature near  $T_c$ , Ginzburg writes:  $\alpha = (\partial\alpha/\partial T)_c(T - T_c)$  and  $\beta = \beta(T_c)$ . The free energy in zero field is then  $F_{SO} = F_{NO} - (\alpha^2/2\beta)$ . But we know the free energy difference,  $F_{NO} - F_{SO}$ , equals the magnetic energy density at the critical field,  $H_c^2/8\pi$ . Thus they find:

$$H_c^2 = \frac{4\pi\alpha^2}{\beta} = \frac{4\pi(d\alpha/dT_c)(T - T_c)^2}{\beta_c}.$$

The shape of the magnetic critical field vs. temperature is experimentally similar to the above expression. Of course, we now recognize that much of this resembles the old Gorter-Casimir (74, 75) two fluid theory of superconductivity dressed in new symbols and carrying on further. The field depth of penetration from the London theory now becomes (in weak fields)

$$\delta_0^2 = \frac{mc^2\beta}{4\pi e^2|\alpha|}.$$

In strong fields they (73) find (for the one dimensional case above):

$$\delta = \delta_0 \left\{ 1 + \frac{e(\epsilon + 2\sqrt{2})}{8(\epsilon + \sqrt{2})^2} \left( \frac{H}{H_c} \right)^2 \right\}$$

where the quantity

$$\epsilon^2 = \frac{1}{2\pi} \left( \frac{mc}{e\hbar} \right)^2.$$

The quantities  $\alpha$  and  $\beta$  are determined for any superconductor by the characteristic values for that metal of  $\delta_0$  and of  $H_c$ . The quantities calculated (70) are in fair agreement with experiments for Al but not for Sn.

Cullwick (76) has applied electrodynamics to a superconducting sphere and claims that there is no surprise whatsoever in the Meissner effect! He asserts that his new theory gives the basic equations of the London theory (71) and we assert that Professor Cullwick is too optimistic. He has used London's result that the sphere viewed from great distance,  $r > R$ , is simply a dipole of magnetic moment

$$M = \frac{2\pi R^3 B_0}{\mu_0} \quad \text{amperes} \times m^2$$

where  $R$  is the radius of the sphere,  $B_0$  is the applied external field in webers/ $m^2$ , and  $\mu_0$  is the magnetic permeability of the metal ( $12.57 \times 10^{-7}$  weber/amp.-m). Cullwick then divides this magnetic moment by the volume of the sphere,  $4/3 \pi R^3$ , and says the magnetic moment per unit volume inside the sphere is:  $3B_0/2\mu_0$ . Inside the sphere a unit volume sees no magnetic field,  $B=0$ , and has zero magnetic moment per unit volume. Section 4 of Cullwick's paper may convince engineers but we do not find proof that free electrons in a magnetic field "will settle into free stationary orbits" and that they "will then form steady current whose magnetomotive force is easily seen to oppose the applied field." Sondheimer & Wilson (77) have been among the most recent to work on such a problem and superconductivity (Meissner effect) does not fall out of the theory. In other words, we do not see that Cullwick has shown that the currents responsible for the Meissner effect are easily understood.

#### SPECIFIC HEATS

*Calorimetry.*—The Eleventh Annual Calorimetry Conference was held at Johns Hopkins University during September, 1956, and for two days about one hundred scientists from all over the world discussed experiments and theory. Of course, problems of thermometry were discussed and our remarks in the first section of this review will perhaps serve to cover that part of the conference. Rayne & Kemp (78) from Australia discussed heat capacity measurements on dilute copper alloys, and for pure copper gave results which agree with those of Corak *et al.* (79). In the temperature region for  $1^\circ$  to  $5^\circ K$ . these latter authors have shown that copper, silver, and gold have an atomic heat composed of two terms:

$$C = \gamma T + \beta T^3$$

$$\text{where } \beta = (12/5)\pi^4 R/\theta^3.$$

The linear term is due to conduction electrons and the term which is cubic in temperature is the low temperature approximation to the lattice heat capacity of a solid. Corak *et al.* (79) give the following atomic heat constants calculated from a corrected temperature scale between  $1^\circ$  and  $5^\circ K$ .

	Cu	Ag	Au
$\gamma$ (millijoules-mole $^{-1}$ deg. $^{-2}$ )	$0.688 \pm 0.002$	$0.610 \pm 0.005$	$0.743 \pm 0.014$
$\theta^\circ K$ .	$343.8 \pm 0.5$	$225.3 \pm 0.2$	$164.57 \pm 0.14$

These calorimetric measurements have certainly demonstrated great precision and they have confirmed the viewpoint that the electronic and lattice terms may be separated. Berg & Morrison (80) from Canada have reported on the specific heats of some alkali halides between  $2.5^\circ$  and  $270^\circ K$ . Comparing their experimental results with the simple Debye theory of atomic heat [see the very excellent treatment of this theory by Jules De Launay (81)], the variation of the Debye  $\theta$  with temperature is considerable. They

report a minimum value of  $\theta$  at about 10°K. for the salts NaI, KI, and KBr. Only well below 2°K. do these salts enter the true  $T^3$  region according to the evidence presented by Wilks & Webb (82). Probably the time has come for scientists to abandon the technique of presenting their data in terms of the Debye  $\theta$  vs. temperature. Except for the case of some of the elements, and except for very low temperatures, the Debye theory is an over-simplification. Incidentally, a very complete and excellent job has been done by Stull & Sinke (83) in tabulating for the 92 elements the thermodynamic properties such as heat capacity, absolute entropy, heat of melting, and a dozen other properties. Returning now to the specific heat work on copper where the Debye  $\theta$  was determined in the true  $T^3$  region for lattice vibrations, these measurements are supported by the excellent studies of Overton & Gaffney (84) on the temperature variation of the elastic constants of copper. The calculated value of the Debye  $\theta$  from elastic constants (at 2°K.) agree with the heat capacity studies. De Launay (81) has done an excellent job of describing the theory and experiment for just this case and he has introduced what he calls "the electron effect." His latest work (85) extends the work to C, Ge, and Si. We call attention to the work by Catalano & Stout (86) on the thermal anomalies associated with antiferromagnetic ordering in the compounds: FeF<sub>2</sub>, CoF<sub>2</sub>, and NiF<sub>2</sub>. Stephenson & Morrow (87) found a magnetic transition in potassium ferricyanide through heat capacity studies. In Holland similar work has been done on paramagnetic alums by Kapadnis (88). The heat capacity of dysprosium shows magnetic transitions at temperatures where there is a maximum in the heat capacity (89).

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# SOLUTIONS OF ELECTROLYTES AND DIFFUSION IN LIQUIDS<sup>1</sup>

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## SOLUTIONS OF ELECTROLYTES

This review reflects the interests of the authors in that it deals principally with the topics of thermodynamics, conductance, and diffusion in electrolyte solutions. However it seemed desirable to include in the discussion of diffusion data a treatment of diffusion in liquid systems generally, since the fundamentals of the problem are the same for both molecules and ions. Since the last issue of this Review did not include the usual section on electrolyte solutions, the coverage has been extended to include work published during 1955; on the other hand, delays in the arrival of journals from Europe and the United States have made it impossible to cover some of the later publications during 1956.

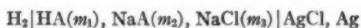
The period under review has not been one of outstanding original advances, but substantial progress has nevertheless been made, particularly in the fields of ionic solvation and in the conductance of electrolytes in concentrated solutions and in nonaqueous and mixed solvents.

### CHEMICAL POTENTIAL

*Activity coefficients of electrolytes.*—The assignment of values for the activity coefficient of an electrolyte at 0.1 *M* when osmotic coefficient data are known only from this concentration upwards has given difficulty in the past. Guggenheim & Turgeon (1) have now revised the values of  $\beta$  in the equation:

$$\ln \gamma = -A\sqrt{m}/(1 + \sqrt{m}) + 2\beta m$$

for the activity coefficient of a 1:1 electrolyte, using recent experimental data at 0° and 25°C. They then study published values of the emf's of the cell:



where A = formate or acetate, the equation for which is:

$$F(E - E^\circ)/RT + \ln m_1 m_3 / m_2 = -\ln K - \ln \gamma_{\text{Cl}} / \gamma_{\text{A}}$$

It is usual to plot the function on the left hand side against the total ionic strength in order to obtain *K* by extrapolation, but little attention has been

<sup>1</sup> The survey of literature pertaining to this review was completed in October, 1956.

paid to the slope of these plots which clearly depend on the variation of  $\ln \gamma_{Cl}/\gamma_A$  with the total ionic strength and which can be expressed in terms of the  $\beta$  coefficients for sodium chloride and sodium formate (or acetate). Having first shown that their  $\beta$  values are in full accord with the experimental data, Guggenheim & Turgeon then reverse the procedure and from available data for the cell:



whence follows  $\beta_{ROH}$  and then the osmotic coefficients at 0.1 *M* of lithium, sodium, potassium, and cesium hydroxide. Now in the compilation of osmotic and activity coefficient data by Robinson & Stokes (2), one of the greatest difficulties was the assignment of values at 0.1 *M* for the hydroxides. It is now apparent that the values given for sodium, potassium, and cesium hydroxide were not greatly in error, but for lithium hydroxide the osmotic coefficient at 0.1 *M* should be 0.894 rather than 0.920, and the data at higher concentration require recomputation.

Little interest has been taken in the glass electrode as a precision instrument since the work of MacInnes and his colleagues (3, 4) but Covington & Prue (5) have now made a significant advance by constructing their electrodes of the Type 9000 of the Jenaer Glaswerk Schott und Gen., Landschut, Bavaria; no amplifying device was needed, the potentials being measured with the usual potentiometer set-up and, although a small, time-dependent, asymmetry potential was present, a simple technique was devised to account for it. Measurements with hydrochloric acid as the cell liquid gave results in good agreement with the precise data of Hills & Ives (6) and the method should be applicable in a wide field. In passing, it may be noted that, while

Hills & Ives found the calomel electrode to be satisfactorily reproducible, there has been a growing belief that this is less true of the silver-silver chloride electrode, and it has been recommended (7) that each individual electrode be standardized in an aqueous solution of 0.01 *M* HCl. This warning is particularly timely in view of the many determinations being made of the standard potentials of the  $H_2|HCl|AgCl, Ag$  cell with mixed solvents, e.g., isopropanol (8), propanol (9), acetone (10), and the glycols (11) or with pure solvents such as methanol or ethanol (12).

The method of obtaining osmotic and activity coefficients by isopiestic vapor pressure measurements has been used by Scatchard & Breckenridge (13) for a number of sodium and potassium phosphates and arsenates; by Robinson (14) for thorium chloride; by Biggs, Parton & Robinson (15) for lead nitrate and lead perchlorate; by Miller & Sheridan (16) for sodium thiocyanate, sodium iodide, and sodium perchlorate; by Patterson, Tyree & Knox (17) for gallium perchlorate; and by Bonner and his colleagues (18, 19) for several substituted benzenesulfonic acids. The last mentioned constitute part of an interesting program of work in which models are being sought for ion exchange resins, and in which measurements on mixtures of these sulfonic acids and their salts, it is hoped, will elucidate the equilibria between

a resin and an aqueous solution. As in all problems involving mixtures of electrolytes, the attack cannot be simple but the project is one whose development will be awaited with interest.

The work on gallium perchlorate has revealed that this salt has a high activity coefficient even in concentrated solution, and from this it is reasonable to suppose that the gallium ion is considerably hydrated and the salt completely dissociated in solution. Stokes & Levien (20) came to a similar conclusion about magnesium and zinc perchlorate, and it seems common practice, especially in spectrophotometric work, to regard perchlorates of polyvalent cations as exempt from the difficulties which arise when other salts, more susceptible to ion pair formation, are used. This may well be true for most polyvalent metal perchlorates, but it should be noted that spectrophotometric evidence has been found by Heidt & Berestecki (21) for the existence of  $\text{CeClO}_4^{++}$  ions in cerous perchlorate solutions, with a dissociation constant of 0.012. Of the common electrolytes, our knowledge of sodium carbonate is meagre, but Taylor (22) has now made an extensive study of this salt, partly by emf. measurements of the cell  $\text{Na-Hg}|\text{Na}_2\text{CO}_3|\text{Ag}_2\text{CO}_3, \text{Ag}$  and partly by vapor pressure measurements.

Morton, Campbell & Ma (23) have adapted the isopiestic method to permit the micro-determination of molecular weights using as little as 3 mg. of material, and Levien (24) has considered the problem which arises when isopiestic measurements are made on an incompletely dissociated electrolyte, citric acid in this case, and allowance has to be made for the presence of a small proportion of ions before the osmotic coefficient of the undissociated molecules can be evaluated.

The isopiestic method is dependent on a set of vapor pressure data for a few reference electrolytes, usually sodium or potassium chloride, for which a table of "best" values was compiled some years ago (25, 26, 27), or sulfuric acid for which a tentative table has been adduced (28, 29). These have recently received support by a number of methods. Brown & Delaney (30, 31) devised a method for measuring the vapor pressure of a solution, isolating it from the pure solvent by means of a sensitive bellows pressure gauge, maintaining the solution at 25°C. and lowering the temperature of the solvent until the vapor pressures of solvent and solution were equal. Their results for potassium chloride solutions, those at high concentrations being particularly important, are in excellent agreement with those suggested earlier. Furthermore, Smith, Combs & Googin (32) have used the dynamic method to measure the vapor pressures of sodium and potassium chloride solutions at 30°C., and the small difference between their results at 30°C. and those tabulated for 25°C. (on an average about 0.001 in  $a_w$ ) are consistent with the temperature difference. In the case of sulfuric acid solutions, Hornung & Giauque (33), using the direct manometric method, have obtained results which again support the earlier work, while Glueckauf & Kitts (34) by a technique not unlike that of Brown & Delaney (30) and Stokes (29) have extended the table of values for sulfuric acid solutions to 76 *M*. A welcome ex-

cursion into the field of activity coefficients in nonaqueous solvents has been made by Izmailov & Ivanova (35) who have used amalgam cells to measure the activity coefficients of sodium bromide and sodium iodide up to high concentrations in ethanol and butanol. In both solvents the curve of  $\log \gamma - \sqrt{m}$  passes through a minimum about 0.25 *M* and the curves approach the limiting slope from above.

*Ionization constants of weak acids.*—Work continues on the measurement of ionization constants of weak acids over a temperature range by the Harned-Ehlers method, the following being some that have received attention recently: the acetyl derivatives of  $\alpha$  and  $\beta$ -alanine, glycine, and  $\alpha$ -amino-*n*-butyric acid and also propionylglycine (36), 2-aminoethanol-1-phosphoric acid (37), glucose-1-phosphoric acid (38), glycerol-2-phosphoric acid (39), dimethylethylenediaminediacetic acid and methylaminodiacetic acid (40), ethylenediaminetetraacetic acid (41), nitrilotriacetic acid (42), metanilic acid (43) taurine (44), and the triethanolammonium ion (45). The interest shown in this work in acids of biochemical significance is also to be found in the studies of Pedersen (46) on dihydroxytartaric acid, oxaloacetic acid, pyruvic acid, and tartronic acid.

Of the acids whose ionization constants have been measured at one temperature only, McCallum & Emmons (47) have broken new ground by showing that the nitrate group is particularly powerful as a substituent in lowering the *pK* value of an aliphatic acid, the nitrate acid having a *pK* value some 0.6 units less than the corresponding bromo acid. Dippy, Hughes & Laxton (48) have continued their useful conductivity studies on substituted acids with work on the dimethylbenzoic acids, nitro and chloronitro derivatives of benzoic acid and some cyclohexanecarboxylic acid derivatives.

While the conductivity method of measuring an ionization constant has seldom been used except at a single temperature, Ives & Pryor (49) have now obtained accurate data for the monohalogenoacetic acids over the temperature range 15° to 35°C. and Feates & Ives (50) have made what seem to be even more precise measurements on cyanoacetic acid over the temperature range 5° to 45°C. which are of particular interest for the light they shed on the change in partial molal heat capacity on ionization. Several years ago Harned & Robinson (51) showed that the equation:

$$pK = A_1/T - A_2 + A_3T$$

was sufficient to represent the experimental data for most acids within the limits of error inherent in the measurements. Although it corresponds to a linear variation of the change in heat capacity with temperature, this linear variation was not taken as proved; rather was it claimed that the available measurements, over the range 0° to 60°C. at the most, could be represented in this way and this equation with three parameters has proved a useful means of representing succinctly a mass of experimental results. Feates & Ives consider their results for cyanoacetic acid of sufficient accuracy to test this equation critically, and it is now found that the equation does not suffice

to represent the results of experiments of the accuracy achieved with cyanoacetic acid and that the more complicated equations required no longer lead to a linear variation of  $\Delta C_p$  with temperature. Instead,  $\Delta C_p$  has a well-defined maximum at about 25°C. Although the full significance of this finding cannot be clear until more data are available, it is undoubtedly an important result and suggests, somewhat unexpectedly, by an argument too lengthy to be repeated here, that long range ion-solvent forces increase in magnitude with increasing temperature.

*Spectrophotometry of weak acids.*—Technical developments in the design of ultraviolet spectrophotometers have made measurements of absorption spectra comparatively simple, and it has been found that many organic acids have very different spectra in acid and alkaline solution where the absorbing species are presumably the uncharged, undissociated molecules and the negatively charged anions respectively. Measurements of the optical density in very acid solutions, very alkaline solutions, and solutions buffered at a pH near to the pK value of the weak organic acid, therefore, suffice to give the degree of ionization of the acid and, hence, the ionization constant, provided that the activity coefficient can be estimated, a matter which should not give much trouble as measurements can be made at very low concentrations. The spectrophotometer was used by Sager & Siewers (52) to measure the ionization constant of 4-aminobenzophenone by partial neutralisation of the base with hydrochloric acid. The method has received impetus from recent studies at the Bureau of Standards on the pH of buffer solutions, the latest of which include the conversion to modern terms of the pH values of the well-known Clark & Lub's solutions (53) and the provision of a sixth standard (54) in saturated calcium hydroxide solution with a pH of 12.454 at 25°. The spectrophotometric method for measuring the ionization constant of a weak acid seems to offer considerable promise; it would appear to be a method of good accuracy because Bates & Schwarzenbach (55) obtained  $pK=7.15$  for *p*-nitrophenol, and independent work by Robinson & Biggs (56) gave  $pK=7.14_9$ . Moreover, the method can be used for acids whose solubility in water is so small that other methods are inapplicable, and hence, a study of the relation between acid strength and chemical constitution, so often made in the past by comparison of acids in different solvents, can now be made by comparing a series of acids in aqueous solution. As an illustration, we can quote some unpublished measurements on pentachlorophenol (57) for which solutions as dilute as  $2 \times 10^{-5}$  *N* were adequate.

The method is more difficult to apply to a dibasic acid,  $H_2A$ , whose ionization constants are similar in magnitude because, while the extinction coefficients of the  $H_2A$  and  $A^{--}$  species can be measured, there is no direct way of finding that of the  $HA^-$  species. This difficulty, however, has been overcome in an elegant way by Thamer & Voigt (58). A further application worthy of mention is that of Hall, DeVries & Gantz (59) who deduced the ionization constants of the very weak bases, nitroguanidine and nitroamino-guanidine, from the absorption spectra in strong hydrochloric acid solution,

the bases being so weak that it is difficult to see how their ionization constants could have been found in any other way. Vareille (60) has devised a method of utilizing measurements at isosbestic points to determine stability constants of chelate compounds, specifically the ferric-sulfosalicylic acid complexes.

The two ionization constants of each of the three pyridine monocarboxylic acids have been evaluated recently by both spectroscopic and potentiometric methods (61, 62), the original papers expressing the opinion that the acids in the isoelectric form exist as neutral molecules and not as dipolar ions. In other words, the first acid dissociation was taken to be that of the  $\text{=NH}^+$ -group and the second to be that of the carboxyl. The opposite view was expressed by Jaffé (63), who concluded from an application of the Hammett equation (64) that only 2 to 10 per cent of the isoelectric acid existed in the uncharged form, the rest being dipolar ions. The first direct experimental evidence for this view was adduced by Black (65) who compared the ionization constants and spectra of isonicotinic acid with those of its methyl betaine to show that the former behaved as dipolar ions. A similar conclusion has been reached by Green & Tong (66) from a comparison of the spectra of all three acids with their methyl esters and methyl betaines over a wide pH range. The latter authors have also measured the thermodynamic dissociation constants of the acids and their esters and have used the method of Ebert (67) to evaluate  $K_s$ , the ratio of dipolar ions to uncharged molecules. At 25°C. they find  $K_s$  for picolinic, nicotinic and isonicotinic acids to be 15-10 and 25, respectively. Their results indicate that a carboxyl group attached to the pyridinium nucleus is  $10^2$  to  $10^3$  times stronger than benzoic acid, and the acidic function of the  $\text{=NH}^+$ -group is of the order of ten times stronger than in the corresponding methyl pyridines.

*Theories of hydration.*—A considerable advance has been made in the theory of hydration. It may be recalled that in 1948, Stokes & Robinson (68) proposed an equation for the activity coefficient of an electrolyte which allowed for the Debye-Hückel electrostatic ion-ion interaction and for the thermodynamic consequences of ionic hydration. The equation was successful in accounting for the behaviour of many electrolytes and especially the very high activity coefficients observed in concentrated solutions of many electrolytes, but it suffered two defects: (a) the hydration numbers required were in some cases large, and (b) the hydration number of a cation varied with the nature of the anion although it was believed that the anion was unhydrated. These hydration numbers were probably too large because the hydration effect was made to include a number of other effects one of which is the entropy change on mixing molecules of different sizes (69). Longuet-Higgins (70) has dealt with this effect by the method of volume statistics for polymer solutions, and now Glueckauf (71) has extended the treatment to electrolyte solutions. His equations, which contain two parameters, the hydration number and the distance of closest approach of the ions, are remarkably successful in accounting for the activity coefficients of electrolytes, using hydration numbers smaller than those needed by Stokes & Robinson

and showing, for any one cation, only a minor variation with change in the anion species. While some doubt may remain about the possible effect of ions in breaking the structure of water, an effect which would complicate the volume statistics treatment, Glueckauf's work does represent a real advance. It may be possible to reduce Glueckauf's equation to a one-parameter equation if a recent suggestion by Stokes & Robinson (72) relating the hydration number and the distance of closest approach, based upon Alder's (73) concept of "random close-packed volume," should prove valid.

Gillespie & Oubridge (74) have made cryoscopic measurements of the osmotic coefficients of the alkali metal halides in sulfuric acid as solvent and found that the Stokes-Robinson equation holds with solvation numbers between 1 and 4.5. It would be interesting to know if Glueckauf's additional term for the molal volumes is applicable in this case also.

The concept of hydration is used in a different sense by Shoolery & Alder (75) who have measured the shift of the nuclear magnetic resonance frequency in electrolyte solutions. Relative to the pure solvent, these shifts can be positive or negative and are attributed to two opposing mechanisms. When a water molecule comes near an ion and is "solvated," at least one hydrogen bond must be broken in the water network; in this process, the mutually induced dipoles in two water molecules disappear and the electron density around the protons of the solvated water molecule increases. The protons are more shielded, and the resonance shift is therefore negative. At the same time the ions have a polarising effect on the solvent molecules, a positive ion attracting the oxygen of the water molecule, shifting the electrons toward the oxygen atom, while a negative ion attracts a proton of the water molecule again shifting the electrons towards the oxygen atom. In both cases the polarisation effect results in diminished shielding of the proton and, therefore, a positive resonance shift. The experimental data are in accord with these views. The weak electrolyte, mercuric chloride, gives no resonance shift; large univalent ions, whose effect should be predominantly hydrogen bond breaking, give a negative shift; and small polyvalent ions, which would be expected to cause maximum polarisation effect, cause positive shifts. The negative shift is linear in the concentration up to 1 *M* and then increases less rapidly, due, it is thought, to each ion breaking six hydrogen bonds so that above 4 *M* there are few hydrogen bonds left, and a solvation molecule has to be shared by two ions. The positive shift behaves in the same way with change in concentration; this is taken to mean that the polarisation is effective only in the first layer of solvated molecules. Above 1 *M* the diminishing magnitude of the effect is ascribed to ion pair formation, the fall off being particularly marked for zinc chloride and bromide.

#### CONDUCTANCE OF ELECTROLYTE SOLUTIONS

*Experimental techniques.*—While the classical audio-frequency A.C. bridge method due to Jones and Shedlovsky continues to be the main tool in conductance studies, some important developments have been reported. Ives & Pryor (76) describe a double conductivity cell consisting of two parts



with identical electrode dimensions but different separations, permitting the elimination of lead and electrode-polarization resistances by the "four-leads" method familiar in platinum resistance thermometry. Calvert and his collaborators (77) describe an ingenious electrodeless cell in which a toroidal tube containing the electrolyte serves as a single-turn winding linking a current transformer with a voltage transformer, operating on audio-frequency. Electrodeless cells of previous types have required radio-frequency fields and have been unsuited to exact measurements; the transformer-bridge technique should be of great use in the study of highly conducting solutions.

Development of the direct-current method, with a precision of 0.01 per cent, has been reported by Elias & Schiff (78), while Brody & Fuoss (79) describe and test a new design for dipping electrodes suitable for high precision A.C. measurements.

*Theories of conductivity.*—Developments of the theory in the direction of high concentrations continue. Falkenhagen & Leist (80, 81) slightly revise their earlier theory (82) by a more adequate treatment of a boundary-condition in the theory of the relaxation-effect for ions of finite size. Where formerly their relaxation-term was related to that given by Onsager's limiting formula by a factor approximating closely to  $(1+\kappa a)^{-1}$ , they now find the factor  $[(1+\kappa a)(1+\kappa a\sqrt{q})]^{-1}$ . Since this result now agrees exactly with the corresponding first-order relaxation term derived earlier by Pitts (83), those of us who are unable to follow all the mathematical complexities of the respective arguments may hope that finality is achieved. Those whose taste runs to more complicated formulae may prefer the treatment by Fuoss & Onsager (84) whose result for the relaxation-term is Onsager's original limiting expression multiplied by an extremely involved function of  $(\kappa a)$ ; a higher order electrophoretic term is also given. Tables of these functions are promised, and will certainly be needed. The other modification introduced by Falkenhagen & Leist consists of multiplying the  $\Lambda$  value given by their interionic attraction treatment by the relative fluidity  $\eta^\circ/\eta$ . As has been pointed out elsewhere (85, 86), this gives a substantial extension of the range of approximate validity of the equations; for simple 1:1 electrolytes such as lithium or sodium chlorides the formulae give very fair results even at saturation. As far as the use of the new formulae for extrapolation to infinite dilution from the region up to 0.1  $N$  is concerned, it should be noted that they offer no advantages over the simple form proposed by the reviewers (87); although a given value of  $\delta$  gives different  $\Lambda$  values by the several formulae, it is possible to obtain an equally good fit with any of them by slight adjustments to the  $\delta$  value. For concentrated solutions, the viscosity is clearly relevant, but it is by no means certain that the simple proportionality at present assumed is valid. Stokes & Stokes (88) have compared the limiting conductances of a number of electrolytes in water and 10 per cent and 20 per cent aqueous sucrose solutions, finding that though all the conductivities were reduced in approximately the same ratio by a given sucrose content this was considerably less than the ratio of the fluidities of the solvents.



Gellings (89) proposes the empirical equation

$$\Lambda/\Lambda^\circ = (1 - \alpha) \exp\left(-\frac{A\sqrt{c}}{1 + \kappa a}\right)$$

where  $\alpha$  is an empirical constant; agreement is within a few per cent for a number of salts, including higher valence types, up to several normal.

Edwards (90) and Amis (91) have put forward interesting views about the proper ionic radii to be used if Stokes' Law is to be correlated with ionic mobility.

*Experimental results.*—Measurements of conductivity at high concentrations in aqueous solution are receiving increasing attention, which was long overdue. The salts studied include: NaCl and KCl to saturation at 25°C. (91a, 92); NaCNS, NaI, NaClO<sub>4</sub> to saturation at 0° to 50°C. (93); AgNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> to saturation at 180° and 221.7°C. (94); hydrazinium chloride and nitrate to saturation (95); LiCl, NaCl and KCl at 1, 2, and 3 *N* up to 340°C. (96); KBr, NH<sub>4</sub>Cl, and Ca<sub>2</sub>Fe(CN)<sub>6</sub> at 25°C. (77); NaNO<sub>3</sub> and K<sub>3</sub>Fe(CN)<sub>6</sub> to 3 to 5 *N* at 25° C. (89); MgCl<sub>2</sub> and MgSO<sub>4</sub> to saturation at 0° and 25°C. (97). The measurements on magnesium chloride are of particular interest in demonstrating the difficulties confronting any theory of the conductance of polyvalent electrolytes in concentrated solution for, according to some calculations made by the reviewers,  $\eta\Lambda$  is constant over a considerable range of concentration so that neither electrophoretic nor relaxation terms are needed!

In the field of high dielectric constant solvents Gillespie & Cole (98) have confirmed the high dielectric constant of sulfuric acid with  $\epsilon=101$  at 25°C. Two other such solvents, formamide ( $\epsilon=115.5$  at 20°C.) and N-methylacetamide ( $\epsilon=165.5$  at 40°C.) have also received attention and it has been shown (99, 100, 101) that the Debye-Onsager theory, applied so successfully to aqueous solutions, is also valid for these solvents. Thus many electrolytes are completely dissociated as the  $\Lambda - \sqrt{c}$  curves approach the straight line of the Onsager limiting law from above, the nitrates being one of the few exceptions. The hydrogen ion does not have abnormally high mobility so that the proton transfer mechanism does not have to be invoked. Alkali metal ions have mobilities comparable with the Pr<sub>4</sub>N<sup>+</sup> and Bu<sub>4</sub>N<sup>+</sup> ions suggesting some solvation of the former, although the authors do not visualise the solvation as resulting from the formation of a sheath of solvent molecules around the ion, but rather as a distortion of the chain-like, quasi-crystalline structure of the solvent.

At the other end of the scale, the current picture of low dielectric constant solvents as media particularly suited to Bjerrum ion-pair formation is supported by a number of studies. Kraus (102) reviewed the subject at a symposium in Minneapolis in September, 1955, and work on the following solvents is to be noted: *o*-chlorobenzene,  $\epsilon=9.93$  at 25°C. (103); acetic acid,  $\epsilon=6.20$  at 30°C. (104); ethylenediamine,  $\epsilon=12.9$  at 25°C. (105, 106); *n*-propanol,  $\epsilon=20.1$  at 25°C. (107) and acetonitrile,  $\epsilon=36.7$  at 25°C. (108)

while two new solvents have been used, dimethylformamide,  $\epsilon = 36.71$  at  $25^\circ\text{C}$ . and dimethylacetamide,  $\epsilon = 37.78$  at  $25^\circ\text{C}$ . (109 to 112) which seem to be border-line solvents, sodium and potassium halides being completely dissociated in them while quaternary ammonium salts are almost but not completely dissociated. For incompletely dissociated electrolytes, conductivity data give dissociation constants which can be correlated by means of the Bjerrum theory with the distance of closest approach of the two ions, and these distances usually turn out to be of the correct magnitude.

The position is not so happy for aqueous solutions although it is becoming more and more plain that complete dissociation is the exception rather than the rule, and for most electrolytes some interaction is occurring which we call ion-pair formation by analogy with behaviour found in solvents of lower dielectric constant. Thus, for most aqueous electrolytes we are getting back to the Arrhenius picture with the superposition of Debye-Hückel forces. Many experimental results are available, especially as spectrophotometric studies have also been introduced. Davies & Owen (113) have made the chemical curiosity, *tris* triethylenetetramine nickel metaphosphate, a 4:4 electrolyte dissociating into only two ions and yet containing 102 atoms giving a molecular weight of 872. As would be expected, it is a weak electrolyte, comparable in strength with acetic acid. Some ion-pairing takes place in solutions of the sulfate, but the chloride is fully dissociated in contrast to the corresponding sextuply charged cobaltic ion whose chloride is incompletely dissociated (114). In some cases disturbingly large differences in the dissociation constant are found when different methods are used. Thus, Biggs, Parton & Robinson (15) found  $K = 0.027$ ,  $0.017$  and  $0.012$  for the  $\text{PbCl}^+$ ,  $\text{PbBr}^+$  and  $\text{PbI}^+$  ions respectively, using spectrophotometric measurements; a similar method gave  $K = 0.0257$  for  $\text{PbCl}^+$  and  $K = 0.0142$  for  $\text{PbBr}^+$  and extended the measurements to water-methanol mixtures (115, 116). Nancollas (117) from conductivity measurements found  $K = 0.0255$  for  $\text{PbCl}^+$  in good agreement with the other determinations but  $0.037$  for  $\text{PbBr}^+$  which is a startling disagreement! The equation for the dissociation constant contains an activity coefficient term which may be large for polyvalent ions, and this may account for the difference between  $K = 0.037$  found by Nancollas for  $\text{PbBr}^+$  and  $0.077$  found in  $1\text{ }M$  salt solution by Kivalo (118) by a polarographic study, but it is difficult to see why the conductivity and spectrophotometric studies should disagree especially as they agree for  $\text{PbCl}^+$ . A similar anomaly is found with hexammino cobaltic sulphate for which Bale, Davies & Monk (119) found  $K = 11.3 \times 10^{-4}$  by spectrophotometry whereas Jenkins & Monk (120) had earlier got  $K = 2.77 \times 10^{-4}$  by conductivity measurements. On the other hand, we find remarkable agreement with bivalent metal sulfates, the spectrophotometric method (119) giving  $K = 0.0047$  for copper sulfate at  $25^\circ\text{C}$ . while measurements of the freezing point depression give  $0.0046$  (121). Again, Caton & Prue (122) have used the rate of decomposition of diacetone alcohol to measure the hydroxyl ion concentration of solutions of hexamine cobaltic hydroxide and hence the dissociation con-

stant from which, using Bjerrum's theory, they deduce that the ions can approach within  $3.7 \text{ \AA}$  of one another in agreement with the crystallographic value of  $3.9 \text{ \AA}$ . Yet the same reaction had led (123) to the conclusion that the distance of closest approach for thallos hydroxide was  $1.23 \text{ \AA}$  and this has been confirmed by parallel work by Bell & Panckhurst (124) using the rate of neutralization of nitromethane. But this distance of  $1.23 \text{ \AA}$  is much smaller than the crystallographic distance,  $2.8 \text{ \AA}$ . Both Brown & Prue (125) and Caton & Prue (122) have considered the possibility of using a critical distance, outside which no ion pair formation occurs, different to that suggested by Bjerrum. It is shown that if the Bjerrum critical distance is increased by 50 per cent, the data can be reconciled with the crystallographic distance of  $2.8 \text{ \AA}$ . There is no reason to believe that Bjerrum's critical distance is unchangeable, but one is confronted with a difficult situation if the critical distance works in some cases and in others has to be multiplied by a factor which becomes another variable in the theory. Interesting as the possibility is, we must face the fact that we are straining the Bjerrum theory if we apply it to species such as  $\text{TIOH}$  and  $\text{PbCl}^+$  where we have little knowledge of the dielectric properties.

### DIFFUSION IN LIQUIDS

The rapid increase in the number of papers dealing with diffusion in liquid systems would justify a separate review article, but as diffusion and electrolytic conduction have many features in common, the general topic of liquid diffusion is included in the present chapter. Earlier work in nonelectrolyte solutions has been ably reviewed by Johnson & Babb (126), and in electrolyte solutions in the 1955 issue of these reviews.

*Experimental techniques.*—Gosting and co-workers (127, 128, 128a) have developed methods of determining the four diffusion coefficients describing diffusion in a three-component system from the displacements of the interference-fringes in the Goüy method from the "ideal" positions corresponding to a Gaussian refractive index gradient curve.

Creeth (129) develops and tests the theory of both the Goüy and Rayleigh interference methods for the case where the diffusion coefficient varies with the concentration, incidentally confirming the existence of a common point (130) in the refractive index curves for a fixed value of the mean diffusion coefficient  $\bar{D}$  when  $D$  varies linearly with concentration. He also reports that Goüy results are approximately 0.1 per cent higher than Rayleigh-fringe results for the same system. Caldwell & Babb (131) apply the Mach-Zehnder interferometer to diffusion measurements. Nachtrieb and co-workers (132) employ a cell in which the diffusion column is sheared into layers at the end of the run, in self-diffusion measurements with radio-tracers. The magnetically-stirred porous-diaphragm cell continued to yield results of good accuracy (133). White (134) reports a difference of 6 per cent between measurements, in a diaphragm-cell calibrated with aqueous  $\text{KCl}$ , of the diffusion of biphenyl in benzene and those determined by the Goüy method,

which is not surprising since he used unstirred diaphragm-cells. The capillary-tube method of Anderson & Saddington (135) is widely used in self-diffusion and tracer-diffusion studies; Mills (136) shows that discrepancies (137) between this method and the magnetically stirred diaphragm-cell can be eliminated by careful control of the flow-rate of the bath liquid over the open end of the capillary, and by ensuring laminar flow in this region. Harned's conductimetric cell remains the best method of measuring diffusion in dilute electrolyte solutions (138, 139).

*Self-diffusion in pure liquids.*—Isotopic tracer studies with radioactive counting or mass-spectrographic analysis have provided self-diffusion coefficients for the following liquids: Nachtrieb & co-workers: Hg, 0° to 98°C. and 1 to 8000 atm. (132); Na, 98° to 226°C. (139); Ga, 30° to 98°C. and 1 to 10,000 atm. (140); Corbett & Wang, argon at -189°C.—a remarkable experimental achievement (141); Careri & Paoletti, In and Sn 250° to 650°C. (142); Watts, Alder & Hildebrand, CCl<sub>4</sub> 25° to 50°C., 1 and 200 atm. (143); Fishman, *n*-pentane 35° to 79°C. and *n*-heptane 96° to 79°C. (144). In most of these cases the diffusion coefficients and viscosities are found to conform with the relation  $D\eta/T = \text{constant}$  within a few per cent, though references (142) and (144) show departures at extreme temperatures. This relation is of the Stokes-Einstein type  $kT/D\eta = 6\pi r$  but evaluation of  $r$  from it invariably leads to results lower by a factor close to 2 than the known atomic or molecular radii. Eyring's kinetic treatment (145), on the other hand, gives a radius some five times too high, his formula being  $kT/D\eta = 2r$ . Li & Pin Chang (146) reexamine Eyring's approach and suggest the need for different definitions of the molecular velocity in diffusion and viscous flow, arriving at the result

$$\frac{kT}{D\eta} = \frac{2\sigma}{\sigma - \tau} \left( \frac{\bar{V}}{N} \right)^{1/3}$$

where  $\bar{V}$  = molar volume,  $N$  = Avogadro number,

$\sigma$  = number of nearest neighbours in all directions

$\tau$  = number of nearest neighbours in one layer.

The ratio  $2\sigma/(\sigma - \tau)$  has about the needed value when the packing is simple cubic. Nachtrieb *et al.* (132, 139, 140) make the point that in liquid metals the Stokes-Einstein radius is nearly the ionic radius; can the conduction electrons be regarded as providing a hydrodynamic continuum in which the ions move? This attractive idea is at variance with the fact that the Stokes-Einstein radius is 0.59 of the atomic radius for Hg, 0.57 for Argon, 0.49 for Na and Ga, and 0.52 for CCl<sub>4</sub>; the kinetic entity in argon and CCl<sub>4</sub> is certainly not an ion.

Ottar (147) gives a slightly different kinetic approach leading to the equation

$$kT/D\eta = 4\sqrt{2}(\bar{V} \cdot N)^{1/3}$$

which agrees within 10 per cent with most of the self-diffusion data available, except for water, methanol and ethanol, where deviations are excusable. Spornol (148) proposes the empirical correction factor  $(1+r_L^2/r^2)$  to Stokes'-law radii, where  $r_L$ =radius of solvent molecule and  $r$ =radius of diffusing molecule; the factor 2 resulting for self-diffusion would be very convenient.

*Diffusion in binary nonelectrolytes.*—The diffusion of a number of non-electrolytes at low concentrations in various solvents is reported by several workers (133, 149, 150, 151). Some measurements on argon and nitrogen in water as solvent by Smith, Friess & Morales (152), though of relatively low precision (as might be expected in view of the low solubilities), are of great interest. The mobility of argon in water is appreciably lower than that of the ions  $K^+$  and  $Cl^-$  which have the argon structure. Wilke & Pin Chang (153) propose the general empirical correlation

$$D = 7.4 \times 10^8 \frac{(xM)^{1/2} T}{\eta V^{0.8}}$$

for such results, based on an analysis of 251 systems which are fitted within about 10 per cent. Here  $V$ =the molar volume of the solute at the boiling point;  $M$ =molecular weight of solute and  $x$ =an adjustable association parameter. The result, though dimensionally impossible, is clearly of practical value for the approximate estimation of diffusion coefficients for which it is designed. Hill (154), extending to the case of diffusion her concept of the "mutual viscosity" developed for dealing with the dielectric relaxation of polar molecules in liquids, obtains for the limiting diffusion coefficient of A at vanishing concentration in B the result:

$$D = kT/(6\eta_{AB}\sigma_{AB})$$

Here the quantity  $\eta_{AB}\sigma_{AB}$  is a constant for the system, evaluated from the viscosity and density of mixtures. However since exactly the same result is obtained for the limiting diffusion coefficient of B in A, which is contrary to all experience, it is clear that something has been overlooked in this derivation.

Diffusion studies over the whole range of composition are reported for methanol-benzene at 27° (131), carbon tetrachloride-ethanol at 25° (133), and carbon tetrachloride-cyclohexane at 25° (133). Johnson & Babb (155) compare self- and mutual diffusion results in the systems  $CCl_4$ - $C_6H_6$ ,  $EtOH$ - $MeOH$ ,  $MeOH$ - $C_6H_6$  and  $EtOH$ - $C_6H_6$ , while Caldwell & Babb (156) give results for  $C_6H_6$ - $CCl_4$ ,  $C_6H_5Cl$ - $C_6H_5Br$  and  $C_6H_5CH_3$ - $C_6H_5Cl$  over the whole range of composition at 10° to 40°C.

The theory of diffusion in binary mixtures is discussed by Lamm (157), Ping-Yao Cheng (158), Hill (154), Collins & Raffel (159) [see also (126), (155) and (156)].

*Diffusion in aqueous electrolytes.*—Self-diffusion of ions in electrolyte solutions is reported on by Friedman & Kennedy (160); see also (137) and (138), and for a review, (161). It is accepted that the self-diffusion coefficient of an

ion at infinite dilution must be given by the Nernst result  $D_i^0 = \lambda_i^0 RT / (|z| F_2)$ ; and interest, therefore, centres on the concentration dependence of the self-diffusion coefficient. The experimental difficulties which cause marked discrepancies between the results of various workers and techniques are at last being overcome, but the most reliable results are still in the relatively concentrated region where the difficulties of interpretation are greatest. It is to be hoped that the recent successful extensions of the interionic attraction theory of conductance to this region will be followed by similar treatments of the relaxation-effect in self-diffusion.

The study of ordinary diffusion in electrolytes continues. Harned & Parker (162) reinvestigate calcium chloride, a salt which has proved unusually recalcitrant. Vitagliano & Lyons (163) give results from 0.02 *N* upwards for sodium chloride and barium chloride by the Goüy method; agreement with the magnetically-stirred diaphragm-cell results for sodium chloride averages  $\pm 0.2$  per cent up to 2 *N*, but at 3 *N* and 4 *N* the diaphragm-cell results are about 1 per cent lower. Harned, Parker & Blander (164) give data for lithium and potassium perchlorates up to 0.01 *N*, deducing that their activity coefficients up to this concentration are closer together than freezing-point measurements indicate. Some complex ions of cobalt have also been studied (165). Freise (166) points out that the ion-exchange properties of agar gel can affect the values for diffusion in such gels.

Diffusion in acetic acid solutions has been studied by Vitagliano & Lyons (167), who compute from their results the mobility of the undissociated acetic acid molecule, and also find at the other extreme of concentration that the mobility of water in acetic acid is normal (in terms of the Einstein-Stokes radius). Goüy measurements by Brudney & Saunders (168) show the effects of micelle formation on the diffusion of potassium laurate. Philips & Mysels (169) study the self-diffusion of micelles in sodium lauryl sulphate solutions by using an oil-soluble neutral dye to "label" the micelles, arriving at a micellar molecular weight of 20,000 to 30,000 by the application of the Einstein-Stokes relation.

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# SOLUTIONS OF NONELECTROLYTES<sup>1</sup>

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**Introduction.**—The scope of this review has been limited mostly to the work on gaseous mixtures and liquid solutions. Since the most significant new theory presented during 1956 was the extension of the corresponding states principle to multicomponent mixtures, the writer has attempted to include all the publications directly related to this theory. This emphasis has required the omission of comments on several topics among the wide variety of subjects usually reviewed, notably molecular complexing, metallic solutions, transport properties, and general phase equilibria. A general review of diffusion (including nonelectrolytes) is given in the chapter "Solutions of Electrolytes."

## GENERAL THEORY

**Corresponding states theories.**—A corresponding states principle in one form or another has been used for many years, particularly by chemical engineers, in the treatment of multicomponent mixtures. 1956 was a year in which the theoretical chemists rediscovered this concept, and as a result several comprehensive discussions on the subject have appeared. It is perhaps not without interest, however, to review briefly the background of the corresponding states theory before discussing this year's developments.

The numerous empirical equations of state that have been proposed for pure gases and liquids have frequently been applied to mixtures by adopting some type of mixing rule for the parameters or constants that appear in the equation. For example the van der Waals' equation

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \quad 1.$$

is commonly used for mixtures (1) by taking the parameters  $a$  and  $b$  to vary in the following manner with composition,

$$a = \sum_i \sum_j x_i x_j a_{ij}; \quad b = \sum_i \sum_j x_i x_j b_{ij} \quad 2.$$

The  $x_i$  are the mole fractions of the components and the constants  $a_{ii}$  and  $b_{ii}$  are the constants for the pure components. The mixed constants  $a_{12}$  and  $b_{12}$  are obtained from an empirical combining law.

Kay (2) went one step further by introducing the concept of a pseudocritical point of a mixture by considering a pure compound whose  $P$ - $V$ - $T$  relations in the superheated region are identical with those for the mixture. The critical point of this pure compound is called the pseudocritical point of the mixture. If, then, the pressure and temperature of this pseudocritical

<sup>1</sup> The survey of literature pertaining to this review was concluded in December, 1956.

point is known, the  $P$ - $V$ - $T$  relations can be calculated exactly as they would be for a pure compound. Kay first used a graphical method of superimposing data for a mixture over that for various pure substances and looked for a match. Later he proposed the following empirical formulas for calculating the pseudocritical point,

$$T_c = \sum_i x_i T_{ci}; \quad P_c = \sum_i x_i P_{ci} \quad 3.$$

where  $T_{ci}$  and  $P_{ci}$  are the critical temperature and pressure of pure component  $i$ .

In 1947, Joffe (3) pointed out that the assignment of a pseudocritical temperature and pressure to the mixture is entirely consistent with the method of combination of equation of state constants. For example, since the constants in the van der Waals equation are related to the critical constants of the pure substances,

$$a_i = 27R^2 T_{ci}^2 / 64 P_{ci}; \quad b_i = RT_{ci} / 8 P_{ci} \quad 4.$$

we can by analogy define the pseudocritical constants for the mixture by the equations,

$$a = 27R^2 T_c^2 / 64 P_c; \quad b = RT_c / 8 P_c \quad 5.$$

Using the combining laws given in equation 2 one can obtain an empirical rule for the computation of  $T_c$  and  $P_c$ .

These procedures or various minor modifications thereof still dominate much of the practical work on mixtures as the following examples illustrate. Hobson & Weber (4) have made a study of the compressibility factors for both pure substances and mixtures under saturated conditions. The saturation curve can be expressed as a function of reduced pressure and the critical compressibility factor. That is,  $z = pv/RT = f(p_r, z_c)$ , where in the case of mixtures  $P_r = P/P_c$  is obtained using Kay's (2) pseudocritical concept. The systems studied included methane + various hydrocarbons, methane +  $\text{CO}_2$  and methane +  $\text{H}_2\text{S}$ . Canjar & Peterka (5) have presented an enthalpy correlation which can be expected to predict hydrocarbon-mixture enthalpies with a fair degree of accuracy. The method of correlation is by use of the molal-average-boiling point  $= \sum x_i B_i$ , where  $B_i$  is the boiling point of pure  $i$ . It is claimed that when a mixture has the same (M.A.B.P.) as the normal boiling point of some pure hydrocarbon, the  $P$ - $V$ - $T$  as well as the derived thermodynamic functions for the mixture are identical with those of the pure component. Leland (6) has developed a method of defining the pseudocritical values using the exact expression for the second virial coefficient for gases,  $B = \sum_i \sum_j x_i x_j B_{ij}$ , where  $B_{ii}$  is the second virial coefficient for pure  $i$  and  $B_{ij}$  ( $i \neq j$ ), the cross coefficient, is usually computed from some type of combining rule (1). In order to illustrate this we again consider the van der Waals equation, equation 1, which yields a second virial coefficient of the form  $B_{ij} = b_{ij} - a_{ij}/RT$ . Substituting this expression into that for  $B$ , we obtain the combining rules given by equation 2 for the equation of state constants  $a$  and  $b$ . Again this can be expressed in terms of pseudocritical values

using equations 4 and 5. Leland (6) applies this procedure to the two-constant equation proposed by Benson & Golding (7),

$$P = RT/(v - bv^{-1/2}) - a/T^{2/3}b^{2/3} \quad 6.$$

to obtain the combining rule

$$b^{2/3} = \sum_i x_i x_i b_{ii}^{2/3}; \quad ab = \sum_i \sum_j x_i x_j a_{ij} b_{ij} \quad 7.$$

The reviewer wishes to remark at this point that for a general equation of state, the second virial coefficient may be a complicated function of the temperature. For such a case, the average constants  $a$  and  $b$  will be functions of the temperature as well as the composition and the parameters  $a_{ij}, b_{ij}$ .

Scott (8) has called attention to the fact that the recent molecular theories of solutions [Prigogine & Mathot (9); Salsburg & Kirkwood (10); Longuet-Higgins (11)] use a theory of corresponding states to deduce the properties of solutions from theoretically derived properties of the pure components. On the basis of these developments, Scott (8) presents a more general corresponding states treatment that can be used with an experimental equation of state for the pure liquid. He discusses three alternative ways of explicitly introducing the corresponding states law. They are referred to as (a) the "single liquid" solution, (b) the "two liquid" solution, and (c) the "three liquid" solution. The work covered in part (b) has also been carried out independently by Prigogine, Bellemans & Englert-Chwoles (12).

Method (a) is formally equivalent to the empirical work of Kay (2). The excess Helmholtz free energy and thus the derived thermodynamic functions are expressed as universal functions,

$$A'/RT = A'(\tilde{T}, \tilde{v}) \quad 8.$$

of a reduced temperature  $\tilde{T}$  and reduced volume  $\tilde{v}$ ,

$$\tilde{T} = kT/\epsilon_m; \quad \tilde{v} = v/N(r_m^*)^3 \quad 9.$$

where the characteristic temperature  $\epsilon_m/k$  and characteristic volume  $Nr_m^{*3}$  are functions of the composition and the corresponding parameters for the pure fluids.  $\epsilon_m$  and  $r_m^*$  are the usual molecular potential parameters and they can be related to the critical parameters of the fluid (1). From one point of view the "single liquid" procedure presented by Scott (8) is another method for the computation of the pseudocritical parameters. However, since it is based upon a molecular theory it provides a deeper insight into the nature of the approximations involved than do the methods mentioned above. Scott gives the basis for a general derivation in his appendix I. The presentation is given in terms of the statistical mechanical expression for the configurational part of the Helmholtz free energy,  $A'$ , of a mixture of  $N_1$  molecules of type 1,  $N_2$  molecules of type 2,  $\dots$ ,  $N_c$  molecules of type  $c$ .

$$A' = -kT \ln Q$$

$$Q = \int^v \exp [-\beta U] d\tau \quad \beta = 1/kT \quad 10.$$

where  $U(r_1^1, \dots, r_{N_1}^1, r^2, \dots, r_{N_2}^2, \dots, r_{N_c}^c)$  is the potential of intermolecular force and is usually approximated by the sum of pair potentials,

$$U = \frac{1}{2} \sum_i \sum_j \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} u_{ij}(r_i^i, r_j^j) \quad 11.$$

The important point to note about the potential for mixtures is that it is not symmetric in the interchange of any two vector positions  $r_i$  and  $r_j$ . That is, for an arbitrary configuration, the value of  $U$  depends upon the type of molecule associated with each position. However, in the evaluation of  $Q$  the position vectors are just variables of integration and since each integration is carried out over the entire physical volume,  $v$ , the value of  $Q$  is independent of the way we have assigned molecules to positions in equation 11. Thus we may write

$$Q = \frac{1}{p} \sum_p \int^\nu e^{-\beta U} d\tau = \int^\nu e^{-\beta \Phi} d\tau \quad 12.$$

$$e^{-\beta \Phi} = \frac{1}{p} \sum_p e^{-\beta U}$$

where the sum is carried out over all permutations of two kinds of molecules among the fixed positions and  $p$  equals the number of permutations. As a result we obtain  $\Phi$ , a pseudo single component potential function, which has the property of being symmetric in the interchange of any two molecules.

The function  $\exp[-\beta \Phi]$  is just the unweighted average of  $\exp[-\beta U]$  over all permutations. The single liquid approximation, as noted by Scott, consists of replacing  $\exp[-\beta \Phi]$  by  $\exp[-\beta \langle U \rangle]$  where

$$\langle U \rangle = \frac{1}{p} \sum_p U = \sum_{i < j} \phi_{ij} \quad 13.$$

$$\phi_{ij} = \sum_i \sum_j x_i x_j u_{ij}(r_{ij})$$

For each intermolecular distance  $r_{ij}$  we obtain a pseudo pair potential  $\phi_{ij}$ . This is equivalent to the so-called random mixing approximation in the order-disorder theory of solids and for an appropriate form of the pair potential  $u_{ij}$ , e.g.,

$$u(R) = 4\epsilon \left\{ \left( \frac{\omega}{R^3} \right)^4 - \left( \frac{\omega}{R^3} \right)^2 \right\}; \quad \omega = r^* \sigma, \quad 14.$$

one obtains a corresponding states theorem in which  $\phi_{ij}$  has the same form as  $u_{ij}$  with average molecular parameters  $\epsilon_m$  and  $\omega_m$ . For the functional form given by equation 14, this procedure yields

$$\epsilon_m = \left[ \sum_i \sum_j x_i x_j \epsilon_{ij} \omega_{ij}^2 \right]^2 / \sum_i \sum_j x_i x_j \epsilon_{ij} \omega_{ij} \quad 15.$$

$$\omega_m^2 = \sum_i \sum_j x_i x_j \epsilon_{ij} \omega_{ij}^4 / \sum_i \sum_j x_i x_j \epsilon_{ij} \omega_{ij}$$

The "two liquid" solution approach to the corresponding states principle gives a new and important extension to the previous methods. It has been formulated independently by Scott (8) and Prigogine, Bellemans & Englert-Chwoles (12). The basic concept is introduced as an assumption but is obtained by analogy from the earlier cell theories of Prigogine & Bellemans (13) and Pople (14) in which one type of cell was introduced for each component of the mixture. In general the free energy per mole is assumed to have the form,

$$A = A_{\text{ideal mixing}} + \sum_s x_s(\tilde{T}_s, \tilde{v}_s) \quad 16.$$

where  $\tilde{T}_s$  and  $\tilde{v}_s$  are the reduced temperature and volume characteristic of the surroundings of a molecule of type  $s$ . In addition to the additivity of the free energies it is assumed that  $A_s$  is a universal function independent of  $s$ . That is

$$A_s = A(\tilde{T}_s, \tilde{v}_s) \quad s = 1, \dots, c; \quad \tilde{T}_s = kT/\epsilon_s; \quad \tilde{v}_s = v_s/Nr_s^{*2} \quad 17.$$

The mean parameters  $\epsilon_s$  and  $r_s^*$ , which are measures of the mean potential acting on a molecule of type  $s$ , are explicitly taken from the cell theory for a Lennard-Jones 6-12 pair potential.

$$\epsilon_s = \left[ \sum_i x_i \epsilon_{si} \omega_{si}^2 \right]^2 / \sum_i x_i \epsilon_{si} \omega_{si} \quad 18.$$

$$\omega_s^2 = \sum_i x_i \epsilon_{si} \omega_{si}^4 / \sum_i x_i \epsilon_{si} \omega_{si}^2$$

In the theory outlined by Prigogine (12) a different volume,  $v_s$ , is assigned to each species. This is a direct consequence of his corresponding cell theory in which the cell volume varies with the type of molecule occupying the cell. In Prigogine's presentation for a binary mixture a relation between  $v_1$  and  $v_2$  is determined by minimizing the free energy. By adopting a suitable approximation for the molar volume,  $v$ , of the solution he is then able to show that both components are at the same pressure. Scott (8) gives his presentation in terms of the Gibbs free energies with  $T$  and  $p$  as his independent variables. He treats the "two liquids" at the same pressure and notes then that they have in general different molar volumes.

This point would appear to present a major obstacle to a derivation of this theory from the basic principles of statistical thermodynamics in terms of well defined approximations, since temperature and volume would enter as the natural independent variables in such a derivation.

Rice (15, 16, 17) has examined the approximation embodied in equation 16 in some detail. In the first article (15) he considers the effect of holes on the cell model for solutions. Using a random mixing approximation for the distribution of occupied and unoccupied cells, he was able to compute a correction term to the additivity of the free energies. Using the equilibrium number of holes as determined by minimizing the free energy, Rice finds that

the deviation from additivity is only about 4 per cent. In two other articles (16, 17), Rice examines the additivity hypothesis from the point of view of the cell-cluster theory (18). He proposes that an extension, suggested by the cell-cluster structure, of the additivity hypothesis (equation 18) could be obtained by defining a series of reduced temperatures and reduced volumes corresponding to single-cell clusters, double-cell clusters, etc. Rice's general hypothesis is then written in the form

$$A = A_{\text{ideal}} + \{N_1 A_1(\tilde{T}_1^{(1)}, \tilde{v}_1^{(1)}) + \dots + N_s A_s(\tilde{T}_s^{(1)}, \tilde{v}_s^{(1)})\} \\ + \{\eta_1^{(2)} A_1^{(2)}(\tilde{T}_1^{(2)}, \tilde{v}_1^{(2)}) + \dots + \eta_s^{(2)} A_s^{(2)}(\tilde{T}_s^{(2)}, \tilde{v}_s^{(2)})\} + \dots \quad 19.$$

where  $N_s$  is the number of molecules of species  $s$  and  $\eta_s^{(x)}$  is the number of clusters of size  $x$ . The author suggests (16) that this expression may be exact provided only that there is random mixing, and is a statement of a principle of corresponding states for solutions and components.

This comment deserves some clarification. In the first place, the author has not presented a clear statement of the meaning of the subscript  $s$  on  $\eta_s^{(x)}$ . Since more than one type of molecule may be found in a general cell cluster it is difficult to conceive of a number of clusters being associated with a given species. Therefore, it may be reasonable to define  $\eta_s^{(x)}$  to be the number of clusters of a given composition. It is also instructive to examine the limit of 1 cluster containing  $N$  molecules in which the cell-cluster theory becomes exact. As we have seen, the basis for the formulation of the reduced temperature and volume in this case, with the assumption of random mixing, is contained in the article (8) by Scott. The specific formulation of the reduced temperature and volume for a general cell cluster is still in need of clarification. Finally, it should be remarked that no mention is made about the functional form of the various  $A$ 's introduced by equation 19. Specifically, Rice states that this is equivalent to the physical process in which the components are subjected to hypothetical experiments until they are in a state in which their reduced temperatures and volumes are equal to the reduced temperatures and volumes characteristic of their environment in solution. The properties of the mixture are then computed to any desired accuracy by simple addition. This implies that all the  $A$ 's possess the same functional form which is a surprising characteristic and deserves some detailed comment. Many such questions arise in reading these articles, and it is hoped that a clarification and more detailed discussion of this concept will be presented in the near future.

We return now to the article by Scott (8) where still another prescription for a corresponding states calculation of the properties of the solution is introduced. This assumption can be expressed in the form

$$A = A_{\text{ideal mixing}} + \sum_i \sum_j x_i x_j A_{ij}(\tilde{T}_{ij}, \tilde{v}_{ij}) \quad 20.$$

Scott notes that this formulation is similar to the second virial coefficient analysis of gases and probably underestimates the free energy of the solution. No detailed calculations are carried out using this prescription.



Rather than try to estimate the functional form of the  $A$ 's introduced in each of these formulations, both Prigogine (12) and Scott (8) adopted a procedure, introduced by Longuet-Higgins (11), in which the properties of the mixture are expanded in a Taylor series about a reference species. Using Prigogine's formulation, we choose a reference species  $O$ , in conditions  $\tilde{T}_0$  and  $\tilde{v}_0$ . Then

$$A'(\tilde{T}, \tilde{v}) = A'(\tilde{T}_0, \tilde{v}_0) + \left(\frac{\partial A'}{\partial \tilde{v}}\right)(\tilde{v} - \tilde{v}_0) + \left(\frac{\partial A'}{\partial(1/\tilde{T})}\right)\left(\frac{1}{\tilde{T}} - \frac{1}{\tilde{T}_0}\right) + \dots \quad 21.$$

The derivatives of  $A$  are expressible in terms of the thermodynamic properties of species  $O$ . Only the first order terms in the final result agree with the rigorous expansion given by Longuet-Higgins (11). Scott (8) concludes from this that it is unreasonable to push this expansion beyond second order terms (and it is questionable to go that far). The further details of this expansion procedure and a detailed study of the various parameters introduced in these articles is too involved to be discussed in this review. The reader is referred to the original articles which give very clear presentations of the formal development.

A word should be said about the comparison with experiment. The qualitative agreement between experiment and theory is good. However, as the authors stress, good quantitative agreement cannot be expected from the theory in its present state. The reviewer agrees with Prigogine in his comment that the main interest in this theory does not lie in the numerical agreement with the experimental data but in the possibility of obtaining a deeper understanding of the complex relations between intermolecular forces and excess functions.

*Cell theories.*—Rice (17) has extended De Boer's (18) cell cluster theory to multicomponent mixtures. In principle, this provides an exact expansion for the partition function of the system. In practice, however, only the first two terms of this expansion are amenable to numerical calculation. The author applies the theory to a binary solution truncating the general series after the terms corresponding to cell clusters of two molecules. He also uses a "random mixing" approximation for certain combinatorial factors that occur in the theory. The use of the phrase "random mixing" in this connection is not identical with the usual concept of random molecular mixing. In fact, the cell-cluster theory seems to lead to the consideration of an order-disorder problem on three different levels. First, consider the group of molecules inside a given cell cluster. For a given mean potential field the theory postulates that the cell-cluster partition function can be computed exactly, and, thus, the order-disorder problem of mixing the molecules inside the cell cluster is handled in a rigorous manner. One could use a random molecular mixing approximation (see section on corresponding states) for this cell-partition function and presumably this is what is implied by Rice's general statement that he is treating a system in which the molecules are randomly mixed. The order-disorder problem is again encountered in the computation

of a mean potential field for each cell. Presumably some type of random mixing configuration is chosen for the molecules neighboring the given cell cluster which contribute to the potential field. Finally, in the cell-cluster theory one must consider the number of ways of distributing the given number of cell clusters of given size and shape over the reference lattice. The author uses a "random mixing" approximation for this combinatorial factor, which is just a numerical approximation to a complicated combinatorial problem and is not directly related to the intermolecular forces or the usual random mixing of molecular species.

In addition Rice (17) considers the Kirkwood (19) multiple cell-occupancy theory for mixtures. He extends Pople's (20) method of estimating the effect of multiple occupancy to the theory of mixtures. This procedure of improving the cell theory of mixtures is not as promising as the cell-cluster method since the latter does not neglect correlations in the positions of molecules in neighboring cells.

Van der Waals (21) has used the cell theory to give a statistical mechanical description of clathrate compounds of nonpolar gases. The derivation of this theory is given in terms of the clathrate compounds of quinol but it is equally applicable to gas hydrates. The polar substance (in this case quinol) forms a three-dimensional network which contains roughly spherical cavities. If the cavities are empty this crystalline form is metastable or unstable. However, if a certain fraction of the cavities is occupied by molecules of suitable size, the crystals, in a certain region of temperature and pressure, may be thermodynamically stable. A number of different substances (e.g.  $O_2$ ,  $N_2$ ,  $A$ ,  $Kr$ ,  $Xe$ ) may be trapped in the cavities. The author has assumed that the interaction of the encaged molecules with the surrounding network will be very similar to that proposed by the cell theory for adjacent molecules in a liquid.

Considering a clathrate crystal having one cavity to every  $m$  quinol molecules; a fraction  $y$  of the cavities occupied by molecules of type  $A$ ; and a total number of cavities,  $N$ , the partition is assumed to be approximated by

$$\exp[-\beta A] = \exp[-\beta A^0] \frac{N!}{[Ny]![N(1-y)]} h_A^{Ny} \quad 22.$$

$A^0$  is the free energy of the  $Nm$  molecules in the lattice and is assumed to be independent of the entrapped species  $A$ .  $h_A$  is the partition function of an encaged  $A$  in a cavity. Each encaged molecule is assumed to move in an average potential field independently of the other molecules of type  $A$ . In the formulation given by van der Waals  $h_A$  is evaluated by the Lennard-Jones-Devonshire smoothed potential procedure obtained from the free volume theory of liquids (1).

The chemical potentials of the two substances are given by

$$\begin{aligned} A/kT &= \ln[y/(1-y)] - \ln h_A \\ q/kT &= \mu_q^0/kT + (1/m) \ln(1-y) \end{aligned} \quad 23$$

where  $\mu_Q^0$  = chemical potential of pure quinol in the given crystalline form. Applying the condition for thermodynamic-equilibrium,  $\mu_A$  (crystal) =  $\mu_A$  (gas) an expression for the vapor pressure,  $p_A$  of  $A$  is derived assuming the vapor to be ideal.

$$p_A = kT \frac{\phi_A}{h_A} \frac{y}{1-y} \quad 24.$$

where  $\phi_A$  is the internal partition function of a gaseous molecule  $A$ . The result of a calculation for argon trapped in quinol is used to illustrate this theory. Assuming an experimental value for  $y$  ( $y=0.40$ ) the dissociation pressure of the clathrate was calculated to be 3.30 atm. which is in good agreement with the observed value of 3.45 atm.

The three phase equilibrium of solid quinol, clathrate and gas is also examined in this article. Van der Waals notes that the current discussion of the phase behavior of gas hydrates often is not quite correct since the hydrate is not a phase of fixed composition, but should rather be described as a mixed crystal. This would appear to be a very promising theory for clathrates and should be extended to compounds containing more than one species such as ethane-methane hydrates and compounds with cavities of two different volumes.

*Lattice theories.*—Münster & Sagel (22) have revised the Fuchs (23) theory of solid solutions and applied it to the calculation of the critical temperature for phase separation in solid solutions. The theory is equivalent to the well known Ising lattice theories but is formulated in a completely analogous manner to the cluster theory of real gases. The analogy between vapor-liquid equilibria for one-component and a solid-solid miscibility curve is extremely close. The mathematical criteria for a critical point are identical for both cases. The cluster method in crystals, however, has a real advantage over that for real gases; the analysis for the critical point in the former case can be carried to completion in various orders of approximations. The authors have applied the theory to a plane square lattice and a three-dimensional face-centered cubic lattice. In the first case the results may be compared with the exact solution which is known. An interesting observation by the authors is that the Fuchs series converges best when the lattice packing is most dense. Münster & Sagel (24) have then used the results of the theory in an analysis of the phase diagram for Al+Zn. In connection with this theory it should be pointed out that a very fine analysis of the relationship between the Ursell-Mayer cluster theory and the various approximations to the Ising-lattice problem has been presented by Hijmans & De Boer (25, 26).

Krigbaum (27) has re-examined and revised the lattice model treatment of athermal mixtures as applied to high-polymer solutions. The author describes his procedure as a two-step process in which a growing chain forms an interference with a completed molecule. The description, however, is much more clearly given by the actual analysis. Consider a lattice containing  $N_0$  lattice sites with a coordination number  $z$ , the number of nearest

neighbors. Distributed over the lattice are  $N_1$  solvent molecules and  $N_2$  polymer molecules containing  $x$  segments each. Each segment and each solvent molecule occupies one lattice site. In computing the number of possible configurations for such a system, attention is focused on the number,  $v_{i+1}$ , of ways of adding the  $(i+1)$ st polymer.

$$v_{i+1} = [N_0 - ix][z(1 - f_{i+1})][(z - 1)(1 - f_{i+1})]^{z-1} \quad 25.$$

where  $f_{i+1}$  is the probability that one of the sites available to a given segment  $t$  will be occupied by one of  $i$  polymers already on the lattice. The central problem of this type of calculation is estimating  $f_{i+1}$  (note that the overlap of a polymer molecule with itself is neglected). The author reasons that if a growing chain is to interfere with a previously placed polymer it must proceed through one of the  $qz$  vacant first neighbor sites, of the given polymer. (The parameter  $q$  is estimated by using the methods from the theory of order-disorder.) If segment  $(k+1)$  of polymer  $(i+1)$  is to encounter an overlap then segment  $k$  must have entered one of the  $iqz$  vacant first neighbor sites of the  $i$  chains previously placed. Thus using the formulation of a conditional probability,  $f_{i+1} = P_{i+1}Q_{i+1}$ , where  $P_{i+1}$  is the probability that the segment  $k$  will enter one of the  $iqz$  sites and  $Q_{i+1}$  is the conditional probability that if segment  $k$  is in one of these sites segment  $k+1$  then selects the adjacent occupied site. For low concentrations the author uses the approximations

$$P_{i+1} = iqz/(N_0 - ix) \quad \text{and} \quad Q_{i+1} = 1/(z - 1)$$

which are certainly reasonable. He also notes that both  $P_{i+1}$  and  $Q_{i+1}$  increase with increasing concentration of polymer and formulates appropriate approximations for these conditions. The result yields values for  $f$  nearly equal to the average value,  $\bar{f}$ , employed in the treatment by Flory (28), and this is offered as an explanation of why the relatively simple expressions of Flory have agreed so well with experiment. The effects of chain bending and branching are also considered.

Using the data in the existing literature plus volume changes on mixing determined by the author, van der Waals (29) discusses the thermodynamic properties of binary mixtures of  $n$ -alkanes of different chain lengths. The energy of mixing,  $U_s^*$ , and the excess entropy of mixing,  $S_s^*$ , at constant volume were calculated and used to test the current quasi-crystalline theories.  $S_s^*$  is much larger than the theoretical predictions. The author finds that both  $U_s^*$  and  $S_s^*$  are almost temperature independent within the range 20 to 50°C. and that the dependence of  $^*$  on the number of carbon atoms in the molecules is in agreement with a simple theoretical model due to Tompa (30). This article also contains a good summary of the available data on mixtures of  $n$ -alkanes and a critical review of the current state of the theory of long-chain molecules.

**Molecular distribution functions.**—Kelbg & Moller (31) have given a presentation of the Born-Green type of theory for the radial distribution functions,  $g_{\alpha\beta}(r)$  for a multicomponent fluid;  $g_{\alpha\beta}(r)$  is the radial distribution

function between molecules of type  $\alpha$  and type  $\beta$  separated by a distance  $r$ . Some of the presentation appears to duplicate earlier work (32) on binary mixtures. The authors use the superposition approximation but fail to mention that as a result of this approximation the equations for  $g_{\alpha\beta}$  and  $g_{\beta\alpha}$  are inconsistent since they are not symmetric in  $\alpha$  and  $\beta$ . Rushbrooke & Scoins (32) have demonstrated that this discrepancy between the two  $g$ 's is reflected in the fourth virial coefficient but not in the second or third. Kelbg & Moller also derive the expression for the equation of state for mixtures in terms of the radial distribution functions and then proceed to consider the application to a fluid of rigid spheres. The resulting integral equation is expressed in the form

$$\begin{aligned} \ln g_{\alpha\beta}^*(r) = & -\frac{\pi}{r} \sum_{\nu} \rho_{\nu} \int_{-a_{\alpha\nu}}^{a_{\alpha\nu}} (a_{\alpha\nu}^2 - x^2) \phi_{\beta\nu}(x+r) g_{\alpha\nu}^*(a_{\alpha\nu}) dx \\ \phi_{\beta\nu}(y) = & y \{ g_{\beta\nu}(y) - 1 \} \\ g_{\alpha\beta} = & g_{\alpha\beta}^* \exp [-\beta u_{\alpha\beta}] \\ a_{\alpha\beta} = & a_{\alpha} + a_{\beta} \end{aligned} \quad 26.$$

where  $a_{\alpha}$  is the radius of a sphere of type  $\alpha$  and  $u_{\alpha\beta}$  is the pair potential between molecules of type  $\alpha$  and  $\beta$ . The authors then state that if the approximation

$$\phi_{\beta\nu}(y) g_{\alpha\nu}^*(a_{\alpha\nu}) = y(\exp [-\beta u_{\beta\nu}(y)] - 1) \quad 27.$$

is substituted into the right hand side of the integral equation (equation 26) and resulting expression linearized in terms of  $g^*$ , exact expressions for the second and third virial coefficients can be simply calculated from the equation of state expression. The reviewer has checked this calculation, and it indeed leads to the correct second and third virial coefficients for rigid spheres with only a few lines of algebra. This is a rather surprising result in view of the arbitrary nature of the above approximation (equation 27). It essentially ignores the correlation effect between molecules of type  $\alpha$  and  $\nu$  and approximates  $g_{\beta\nu}$  by an expression which by itself would give the second virial coefficient correctly. It would be of interest to learn how the authors arrived at this type of approximation.

McLellan & Alder (33) have evaluated the equation of state for a binary mixture of rigid spheres of arbitrary size ratio up to the fourth virial coefficient by using the more conventional radial distribution function development of Rushbrooke & Scoins (32). The important thermodynamic functions are tabulated as well as the changes in these functions upon mixing at constant free volume. Since the superposition approximation is employed the fourth virial coefficient is inexact. The authors have compared this result with the exact fourth virial coefficient for the case where one of the components is a point sphere. The exact value does not lie intermediate between the two values obtained from the solutions of the Born-Green equations (see above discussion) but is greater than both. The authors also note that a purely repulsive potential of interaction (as represented by hard spheres)

would reduce the pressure of an isothermal system when the stopcock connecting two vessels containing pure gases at the same pressure is opened.

Ling (34) has discussed the theory of x-ray scattering by liquid metal alloys in terms of the radial distribution functions for mixtures. His development for mixtures is an extension of the method used by Fournet (35) in the treatment of pure liquids. Fair agreement with the experimental scattering is found.

*Polarization properties.*—Buckingham (36) has developed a theory of the Kerr effect based upon the fundamental principles of statistical mechanics. The theory is an extension of earlier work (37) by the author and is applicable to a dilute solution in which there is no interaction between solute molecules. If the solvent is comprised of spherically symmetric molecules, then the molecular Kerr constant of a nonpolar solute is found to be equal, to a good approximation, to its value in the gaseous state. For strongly polar and anisotropically polarizable solute molecules Buckingham relates the molecular Kerr constant to the apparent solution moment and anisotropy of the solute.

Harris & Brush (38) have presented a statistical mechanical theory of dielectric polarization for fluid mixtures and applications to dilute solutions of polar molecules in nonpolar solvents. It is claimed that neither the Clausius-Mossotti nor the Onsager formulas are applicable and that the frequently used Debye equation for the dielectric polarization of solutions leads to erroneous results even at infinite dilution of the polar molecules. In view of the results, the theory should be examined very closely. The development is based upon the earlier work of Harris & Alder (39) on the polarization of pure liquids, which has been criticized by Fröhlich (40). This criticism has, in turn, been answered by Harris & Alder (41) and by Harris (42), but the reviewer has not had an opportunity to examine these developments in detail.

*Thermodynamics.*—Haase (43) has given a general discussion of the thermodynamics of sedimentation equilibrium and the interrelations between diffusion and sedimentation in binary nonelectrolyte solutions. Many of the results are already well known, but this article demonstrates their common basis in the theory of irreversible thermodynamics.

Li (44) has derived the Clapeyron equation for a multicomponent system in a very simple manner with no restrictions on the number of degrees of freedom. The use of this equation is illustrated with several specific examples.

Schulz & Cantow (45) have written a critical discussion of the relations between the thermodynamic properties of solutions and the temperature variation of the virial coefficients for the expansion of the osmotic pressure. Emphasis has been placed upon high polymer solutions.

#### QUANTUM FLUIDS

Cohen *et al.* (46) have carried out extensive theoretical calculations for gaseous mixtures of para- $H_2$ -ortho- $H_2$ . The properties calculated from quantum statistical mechanics are (a) viscosity and thermal conductivity, (b) coefficients of self-diffusion and of mutual diffusion, (c) thermal diffusion

ratio, and ( $d$ ) second virial coefficient. A spherical potential field was used for the interaction between  $H_2$  molecules and therefore the calculations are valid only for such temperatures where inelastic collisions resulting in rotational excitation are very rare.

Special attention was placed on the dependence of viscosity on the para-ortho concentration ratio. The calculations show that para- $H_2$  has a greater viscosity than normal  $H_2$  in agreement with the measurements of Becker & Stehl (47). The second virial coefficient is about 10 per cent smaller than the experimental value. This discrepancy is attributed to the neglect of the non-spherical character of the real potential field. It is interesting to note that because of the assumed spherical symmetry of the intermolecular potential field no transitions are allowed between the 9 different states in which an ortho-molecule can exist. Therefore, the authors were able to treat "pure" ortho-hydrogen as a 9-component mixture in which the components have equal masses and equal concentrations. Similarly the para- and ortho-hydrogen mixtures were treated as 10-component mixtures.

A very important and exhaustive study of the thermodynamic properties of  $He^3 + He^4$  has been reported by Yeselson & Bereznyak (48). The temperature dependence of the vapor pressure of twenty solutions, with  $He^3$  concentration varying from 0.4 to 90.8 mole per cent, and the dew point for eight mixtures, with 1.9 to 82.4 per cent  $He^3$  was measured. The pressure-composition phase diagrams are given for the temperatures 1.4°K. to 2.6°K. in steps of 0.2°. The agreement with Sommers' (49) data at low concentrations of  $He^3$  is very satisfactory. The experimental procedure involved the measurement of the difference in the vapor pressure,  $\Delta p$ , between the solution with known concentration of  $He^3$  and the pure  $He^4$ . The change in concentration resulting from evaporation of  $He^3$  was neglected, but the authors seem to feel that since the vapor volume was kept small (about 5 cm.<sup>3</sup> compared to 50 to 250 cm.<sup>3</sup> of liquid volume) this error is negligible. The results show positive deviations from Raoult's law over the entire range of concentrations.

Wansink, Taconis & Staas (50) have also studied the ratio of the vapor and liquid concentrations in  $He^3 + He^4$  mixtures. These measurements were performed for very low concentrations of  $He^3$  only at temperatures between 1.2 and 2°K. The experimental technique in such a measurement is carefully analyzed and discussed in this paper. The results, which are also in good agreement with Sommers (49), are compared with several theories that have been proposed. The best agreement was obtained using Mikura's (51) model.

Trikha & Nanda (52) discuss the temperature dependence of the vapor pressures over a solution of  $He^3 + He^4$  from the point of view of the author's (53) model. No reference is made to the recent and more complete data.

Linhart & Price (54) have revised their previous calculation (55) of the specific heat of dilute solutions of  $He^3$  in liquid  $He^4$  from vapor pressure data in view of the recent measurements by Dokoupil and co-workers (56). The agreement between experiment and the second calculation is improved. However, in correcting their calculation the authors discarded Sommers'



(49) data below 1.35°K., and the validity of this data has been confirmed by the measurements mentioned above.

Agarwal (57) has given a brief summary of the various theories that have been applied to the lowering of the lambda point transition temperature in  $\text{He}^3 + \text{He}^4$  solutions. An empirical macroscopic theory for  $\text{He}^3 + \text{He}^4$  mixtures analogous to that given by Heer & Daunt (58) has also been formulated by Agarwal (59). The model is that of a mixture of incompressible "ideal" gases ( $\text{He}^3$  and  $\text{He}^4$ ) which form statistically independent systems. However, instead of using a perfect gas spectrum,  $E = p^2/2m$ , a generalized spectrum of the form  $E = Ap^{1/r}$  is employed where  $A$  and  $r$  are parameters. In order to obtain agreement with the variation of the lambda temperature with concentration the parameter  $r$  was taken as  $r = 1/2(V_3^0/V_4^0)$  where  $V_3^0$  and  $V_4^0$  are the volumes per atom of  $\text{He}^3$  and  $\text{He}^4$  respectively. The lambda transitions are assumed to be connected with the momentum space condensation of  $\text{He}^4$  atoms alone. Thus, the decrease in the condensation temperature of the mixture may be associated with the decrease in the concentration of  $\text{He}^4$  atoms. Several properties including the vapor pressure relations below and above the lambda temperature are derived by the author.

#### MIXTURES OF GASES

Cottrell & Hamilton (60) have described an apparatus for the measurement of the second virial coefficient of gases at pressures less than 1 atm with an accuracy of  $\pm 5 \text{ cm}^3/\text{mole}$ . The method involves a series of  $p$ - $v$  measurements at a known temperature, which avoid the usual contact between the gas and Hg. The error introduced by Hg vapor, which is present in earlier investigations, becomes appreciable at room temperatures and above.

The measurement of accurate second virial coefficients of gaseous mixtures is of primary importance for the present development of the theory of nonelectrolyte solutions. Since one of the major goals of this theory is to calculate the properties of mixtures from the properties of the pure substances it is desirable to formulate a combination rule by which the potential parameters for the interaction between unlike molecules can be calculated from the parameters for like molecules. Ultimately, empirical combination rules of this sort must be based upon accurate second virial coefficient measurements, in particular,  $B_{12}$ , the coefficient of  $x_1x_2$  in the general expansion of  $B$ .

Reuss & Beenakker (61) have outlined an ingenious method to determine  $B_{12}$  from experiments on the influence of pressure on the vapor-solid equilibrium of one of the components. A heterogeneous equilibrium with two components 1 and 2 is considered. Species 1 can exist in the gas phase and solid phase, while species 2 can exist only in the gas phase. Considering the equilibrium first between pure solid 1 and its vapor and then in the presence of the gaseous component 2, one obtains  $\Delta\mu_1(\text{gas}) = \Delta\mu_1(\text{solid}) = \int_{p_{10}}^p v_1 dp$ , where  $p_{10}$  is the vapor pressure of pure 1,  $p$  is the pressure in the two component system and  $v_1$  is the molal volume of solid 1. In general,  $\mu_1$  for the gas can



be expressed as a function of  $T, v$  (the molar volume of the gas) and  $x_1$  (the composition of the gas) [see Taylor & Glasstone (62)]. One can use the virial equation of state in this expression to obtain

$$\Delta\mu_1(\text{gas}) = RT \ln \left[ \frac{d_1}{d_{10}} \right] + 2 \frac{RT}{v} x_2 B_{12} + \frac{3}{2} \frac{RT}{v^2} x_2^2 c_{122} + \dots \quad 28.$$

where  $d_2$ ,  $d_1$  and  $d_{10}$  are the molar densities of 2 and 1 in the gaseous mixture and of pure vapor 1 above solid 1 respectively and where  $d_2 \gg d_{10}$ ,  $d_1$ .

Thus this method gives a direct measurement of  $B_{12}$  but unfortunately is limited in its scope of application. The authors apply the procedure to the data of Dokoupil, Van Soest & Swenker (63) on the systems  $\text{H}_2 + \text{N}_2$  and  $\text{H}_2 + \text{CO}$ . It was also possible to obtain an estimation of the third virial coefficient for  $\text{H}_2 - \text{N}_2$ . Theoretical calculations based on a Lennard-Jones 12-6 potential are also carried out, including quantum mechanical corrections, and compared with experimentally determined values.

Cottrell, Hamilton & Taubinger (64) have used their method to determine the second virial coefficients of equimolar mixtures of carbon dioxide with nitrogen, oxygen, carbon monoxide, argon, and hydrogen at 30, 60, and 90°C. They conclude from their results that the empirical combining rules  $\sigma_{12} = \frac{1}{2}[\sigma_{11} + \sigma_{22}]$  and  $\epsilon_{12}^2 = \epsilon_{11}\epsilon_{22}$  yield values of  $B_{12}$  agreeing with experiment to within the experimental error.

Zaalishvili (65) has collected much of the earlier experimental values of  $B_{12}$  for a variety of gases. Particular emphasis has been placed upon second virial coefficients for hydrocarbon mixtures.

Harper (66) has also reported an investigation of the compressibility factors for gaseous mixtures of helium and carbon dioxide at 30°C. using the Burnett procedure. Second virial coefficients were calculated from the data. No numerical results were reported in this abstract and therefore a comparison with the data of Cottrell and co-workers (64) could not be made.

There exist large variations and discrepancies among the experimental values of  $B_{12}$  reported in the literature. As an example, one can compare the results on the  $\text{H}_2 + \text{CO}$  interaction determined by Reuss & Beenakker (61) with the earlier work by Van Itterbeek & Van Doninck (67).

### LIQUID SOLUTIONS

Of the many experimental techniques used in the measurement of excess chemical potentials or activity coefficients the most common is a study of the liquid-vapor equilibrium used in conjunction with some knowledge about the vapor fugacities. The classical method of carrying out such a study is by means of an equilibrium still. Ridgway (68) has given a review of the advances made in the design of stills since Fowler (69) reviewed the development in 1948. Other modifications are presented in many of the papers reporting liquid-vapor equilibrium data. Baumann (70) has written a general review of many of the empirical and numerical methods of treating experimental data for liquid-vapor equilibrium in binary mixtures.

In many recent investigations, however, an alternative procedure, the

method of total vapor pressure measurements, is being used. The total vapor pressure is determined at a given temperature for a series of liquid compositions, and the necessity of analyzing the gas phase is eliminated. Current results show that the method is capable of giving a relatively high degree of accuracy. Although this procedure is used in many variations the most comprehensive discussion to appear this year was given by Neckel & Kohler (71), in terms of the Gibbs-Duhem equation for constant temperature,

$$-vdp + x_1d\mu_1 + x_2d\mu_2 = 0 \quad 29.$$

where  $x_i$  is the mole fraction of  $i$  in the liquid phase and  $v$  is the molal volume of the solution. The chemical potential of each species can be expressed in terms of  $p, y_i$ , the mole fraction of  $i$  in the vapor, and  $\bar{v}_i$ , the partial molal volume in the vapor. For a given equation of state (e.g.,  $p\bar{v}/RT = 1 + B(T, y)p$ ),  $\bar{v}_i$  can be computed. With the use of the experimental relation between  $x_1$  and  $p$  one can then obtain an explicit differential equation of the form,  $dy_1/dp = f(y_1, p)$ , which can be solved by a numerical method. One of the major difficulties in this integration involves the estimation of the asymptotic slopes of the  $p$  versus  $x$  data. A discussion of the details of the numerical procedure and a bibliography are included in the article. Schulze (72) has also used the method of total vapor pressures and since the experimental points have some scatter at low concentrations he proposes the use of  $\xi = x_1x_2/(\log p - x_1 \log p_1^0 - x_2 \log p_2^0)$  as a function of  $x_2$  as a "smoothing" device to determine the limiting slope. He claims that  $\xi$  is almost exactly linear in  $x_2$  over an appreciable concentration range. In general, the method seems to have been improved since Scatchard's (73) review.

Thorpe & Scott (74, 75) also employed the procedure in a slightly more restrictive form. The total vapor pressure measurements were fitted by the method of least squares to simple analytical expressions obtained from Margules expansions for the chemical potentials of the species in solution. These expressions for the chemical potentials satisfy the constant pressure and temperature form of the Gibbs-Duhem equation. This procedure avoids a direct integration of the Gibbs-Duhem equation but, in effect, neglects any dependence of the activity coefficients in solution on the total pressure. The fact that the analytical expression for the total vapor pressure can be fitted to the experimental results should not be construed as an indication that the resulting activities are correctly obtained. The resulting equation for  $p$  together with the expressions for  $\mu_1$  and  $\mu_2$  should be substituted into the Gibbs-Duhem equation (equation 29) in order to obtain a measure of the error.

Edwards & Brodsky (76) in their investigations of the liquid Cu+Au system have employed essentially the same procedure by measuring total rates of effusion. The activities are computed numerically without the use of analytical forms, but again the pressure dependence of the chemical potentials have been neglected. In this case the authors checked their result by measuring the gas phase compositions. In view of the results obtained it

appears that the method of total rates of effusion is applicable to these systems.

There are several simple systems that are of particular interest from a theoretical point of view, because they have been almost universally adopted as test cases. An important study from this point of view has been reported by Mathot *et al.* (77) for the system carbon monoxide+methane at 90.67°K. The total vapor pressure, the dew point pressure, and the volumes of mixing were studied as functions of the composition. The system shows a positive excess free energy of mixing together with a negative excess volume of mixing. While the simple cell theory for molecules of equal size is in qualitative agreement with these results the quantitative agreement is not as satisfactory. The excess free energy calculated from the regular solution theory is in surprisingly good agreement with experiment, 26.9 cal./mole compared with the measured 28.0 cal./mole for an equimolar mixture. However, the volume of mixing predicted by the regular solution theory has the wrong sign. This experimental study also utilized the measurement of total vapor pressures and fitted the experimental data to an analytical formulation for the activity coefficients containing two arbitrary constants. No mention is made of whether or not the resulting expressions are consistent with the Gibbs-Duhem equation. This should be a standard check in very accurate work of this sort.

Another important system is carbon tetrachloride+benzene which has been restudied by Fowler & Lim (78) under isobaric conditions at 760 mm. Hg and isothermal conditions at 40°C. Mestres (79) has also redetermined the vapor-liquid equilibrium curve under 760 mm. for this system.

Rastogi & Varma (80) have determined the volume of mixing for the system cyclohexane+cyclohexanol in order to test the recent corresponding states theory of Prigogine and co-workers (12). The experimental curve verifies the change of sign in the volume of mixing predicted by the theory. As another test of this theory Jeener (81) calculated the compressibilities from velocity of sound measurement on the system carbon tetrachloride+neopentane. Agreement with the theoretical calculations is fairly good.

The study of fluorocarbon-hydrocarbon mixtures has aroused considerable interest and activity with the view in mind of seeing whether or not these mixtures can be treated by means of a solubility parameter theory. Thorp & Scott (74, 75) have investigated the thermodynamics of the binary systems  $\text{CHF}_3+\text{CF}_4$ ,  $\text{CHF}_3+\text{C}_2\text{F}_6$ ,  $\text{CF}_4+\text{CH}_4$ ,  $\text{CF}_4+\text{Kr}$ ,  $\text{CH}_4+\text{Kr}$ ,  $\text{C}_2\text{H}_6+\text{C}_2\text{F}_6$ ,  $\text{C}_2\text{F}_6+\text{CHF}_3$ , and  $\text{CH}_2\text{F}_2+\text{CHF}_3$ . The authors found that these mixtures exhibit large positive deviations from Raoult's law and the activities are in disagreement with the solubility parameter theory. The possibility of intermolecular hydrogen bonding has been offered as an explanation. A very surprising result is that the system  $\text{CF}_4+\text{Kr}$  also shows abnormally large deviations from Raoult's law. Lewis (82) has studied the properties of the system hexadecafluor-n-heptane+2,2,4-trimethylpentene including a calorimetric measurement of the heats of mixing at two compositions. New-

come & Cady (83) have used the dew point-bubble point technique to study a series of fluorocompounds but the measurements were not sufficiently accurate to calculate the deviations from ideality.

Fastovskii & Petrovskii (84, 85) have studied the vapor-liquid equilibria for the systems argon+nitrogen and krypton+oxygen for a range of pressures. The authors use a modified Van Laar equation to fit their data.

Röck & Schneider (86) have restudied the system cyclohexane+aniline at very small concentrations in view of the criticism raised by Scatchard (73) to the original work of Ebert, Tschamler & Kohler (87). They confirm Scatchard's view and find that  $\ln \gamma_i$  versus  $x_i$  does not show a zero slope as  $x_i$  approaches zero.

Liquid-vapor equilibrium studies in which activity coefficients have been determined have also been published during the year on the following systems: Benzene+bromobenzene [McGlashan & Wingrove (88)]; alcohol+n-heptane [Katz & Newman (89)]; 1,2,4-trichlorobenzene+n-hexane, triethylamine+mesitylene and bromobenzene+cyclohexane [Neckel & Kohler (71)]; alcohol+chlorobenzene [Schulze (72)]; hydrazine+ammonia [Drago & Sisler (90)];  $\text{CCl}_4$ +ortho-cresol, meta-cresol, para-cresol, xylenol 1-2-6, xylenol 1.2.5, xylenol 1.2.4, xylenol 1.2.3., xylenol 1.3.5. and xylenol 1.3.4. [Bono (92, 93); Brusset & Bono (94)]; benzene+acetone [Canjar & Lonergan (95)]; benzene+toluene [Rollet *et al.* (96)]; naphthene+various aromatics [Myers (97)]; 2,2,5-trimethylhexane+ethylbenzene and 1-octene+ethylbenzene [Weber (98)]; methanol+ethanol+acetone [Amer, Paxton & Van Winkle (99)]; acetone+chloroform+toluene [Satapathy *et al.* (100)]; benzene+cyclohexane+isopropyl alcohol [Storonkin & Morachevskii (101)]; acetone+isopropanol+water [Choffe & Asselineau (102)]; dioxane+water [Bacarella, Finch & Grunwald (91)].

The study of the solubility of iodine in normal solvents was an important part of the work which led Hildebrand to formulate his regular solution theory. This study is still very active with the emphasis now being placed upon a careful determination of the thermodynamic properties of these solutions. Glew & Hildebrand (103, 104) have studied the properties of iodine in n-f-heptane. The most surprising feature is the large value of the partial molal volume of iodine at infinite dilution. A similar study was carried out by Reeves & Hildebrand (105) on the properties of bromine in n-f-heptane with similar results. Jepson & Rowlinson (106) measured the thermodynamic properties of iodine in cyclohexane, benzene, fluorobenzene, chlorobenzene, bromobenzene, mesitylene, pyridine, ethyl bromide, ethyl iodide, and diethyl iodide. All but cyclohexane showed evidence of molecular complexes. McLaughlin & Scott (107) determined the properties of iodine and phenanthrene in  $\text{C}_8\text{F}_{18}\text{H}_2$  and compared the two systems  $\text{I}_2 + \text{C}_8\text{F}_{18}\text{H}_2$  and  $\text{I}_2 + \text{C}_7\text{F}_{15}\text{H}$  using the regular solution theory.

*Heats of mixing.*—New designs on adiabatic calorimeters have been reported by Coops, Balk & Tolk (108); Benson, Goddard & Hoeve (109); and by Gorke & Jenckel (110). Noordtziij (111) has determined the heat of mix-

ing for the three binary systems obtained from benzene, cyclohexane, and carbon tetrachloride for a range of temperatures. Particular emphasis is placed upon the temperature dependence of the heats of mixing. The ternary, quaternary, and quinary systems formed by benzene, toluene, cyclohexane, hexane, and heptane have been investigated by Mathieson & Thynne (112). Various empirical equations which enable the heats of mixing of multicomponent mixtures to be predicted from a knowledge of the heats of mixing of the constituent binary mixtures are examined. Brown, Fock & Smith (113, 114) have continued their program on the heats of mixing and have published data on the systems acetonitrile+carbon tetrachloride and nitromethane; nitromethane+carbon tetrachloride and benzene; ethanol+toluene and methylcyclohexane; and isopropanol+benzene.

*Volume of mixing.*—Wood & Sandus (115) have started a program to determine the thermodynamic properties of binary mixtures using isoöctane as a common component. They have reported the volume on mixing at constant pressure for benzene+isoöctane over a temperature range, 20° to 75°C. Connolly (116) has studied the volumes of mixing for the ternary system butane+benzene+cyclohexane, and Sanghvi & Webster (117) investigated the system cyclohexane+*n*-heptane+benzene. Holland & Moelwyn-Hughes (118) have measured the partial molar volumes of the methyl halides in water. Jenkins & DiPaolo (119) have determined the densities of liquid ozone+oxygen mixtures.

*Miscellaneous.*—Duff & Everett (120) have measured the heat capacities of mixtures of benzene with diphenylmethane by measuring  $(\partial T/\partial p)_g$ . They conclude that this method offers no advantages over direct calorimetric measurements.

Interesting experimental studies on solid solutions of the rare gases have been reported by Halsey & Freeman (121, 122). They have measured the thermodynamic properties of the system krypton+xenon over the temperature range 90 to 120°K., obtaining positive deviations from Raoult's law. Applying the strictly regular solution theory the authors note that the difference between the results of the quasi-chemical approximation and the random mixing approximation is very small. This again shows that further refinements of the order-disorder problem are not needed in quasi-lattice theories but rather an analysis of the effect of composition on the vibrational partition function. This problem has been treated by Booth & Rowlinson (123) and should be applied to these data.

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# THE SOLID STATE<sup>1</sup>

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The field of solid state continues to grow both in scope and vigor in truly phenomenal fashion, playing a role of ever increasing importance in chemistry as well as physics. Thus, in a limited review of this sort the choice of material, as dictated by the author's interests, can be expected to be increasingly selective. For example, in this review often only one recent article which contains a reasonable subject bibliography is referenced. The preparation of the present manuscript was made possible by the generous cooperation of many members of this laboratory and it is a pleasure to acknowledge their contribution.

## ADVANCES IN SOLID STATE REFERENCE SOURCES

The number of sources of published information in this field has increased so much in the past year that this in itself merits review.

A second edition of Kittel's text *Introduction to Solid State Physics* (Wiley & Sons, 1956) contains expanded discussion of crystal symmetry and energy band structure, and new material on alloys, semiconductors, photoconductivity, luminescence, and imperfections. *Chemistry of the Solid State*, edited by Garner (Academic Press, 1955), contains review chapters on the chemistry of crystal dislocations, lattice defects in ionic crystals, semiconductivity and magnetochemistry, and discussions of surfaces, action of light on solids, kinetics, oxidation, chemisorption, and catalysis. *Elektronische Halbleiter*, by Spenke (Springer, 1956), presents the views of the Schottky school on conduction phenomena, including a qualitative description of semiconduction and rectification, followed by an advanced treatment of semiconductor physics.

A major event is the appearance of the new *Handbuch der Physik* (Springer, 1955). Under the general editorship of Flugge, Volume 7 offers complete and up-to-date reviews on crystallography, mechanical and thermal properties of crystal lattices, theory of lattice imperfections, and specific heat of solids. Volume 19 includes reviews on electronic structure of solids, on metallic conductivity, on electric and thermal conductivity, and on photoconductivity. Volume 24 has reviews on the production of low temperatures, on electric conduction, on thermal conductivity, and on specific heat. Material from the 1954 Photoconductivity Conference (sponsored by the University of Pennsylvania, Radio Corporation of America, and the U. S. Office of Naval Research) has appeared in a volume

<sup>1</sup> The survey of literature pertaining to this review was completed in January, 1957.

<sup>2</sup> Division of Union Carbide Corporation.

under the general editorship of Breckenridge (Wiley & Sons, 1956); sections deal with phenomenological theory, photon absorption processes, electron processes, photoconducting materials, and current topics.

Several new periodicals have been established. *The Journal of Electronics*, now in Volume 3, under the editorship of Thomson and with an international advisory board, is intended to cover "electron science—interpreted to mean the description of the behavior of electrons in the free state or in states when their binding energy is low." Coverage to date has been largely British; emphasis has been on solid state devices and on new materials. First appearing in September-October, 1956, the new *Physics and Chemistry of Solids* is edited by Brooks, again with an international advisory board. Devoted exclusively to solid state science, the journal will publish theoretical and experimental papers dealing with original fundamental research in the solid state.

When a subject develops rapidly and branches out into other established disciplines, the need for review articles offering critical digests of work reported in numerous and widely-scattered journal references is acute. It is being met by various review series. Among the newer series is *Solid State Physics; Advances in Research and Applications*, edited by Seitz and Turnbull (Academic Press, 1955-56). Two volumes have appeared. Volume 1 is largely theoretical in scope, dealing with the quantum mechanics of electrons in metals; Volume 2 includes articles on magnetic resonance, on neutron diffraction, on specific heat, plus a detailed report on radiation effects. The new Volume 7 of *Advances in Electronics and Electron Physics*, edited by Marton (Academic Press, 1956) shows a stronger emphasis on solid state physics than was the case in earlier volumes, with articles on the physics of semiconductor materials, on the electrical properties of germanium and silicon, and on energy losses of electrons in solids.

An entirely new series *Progress in Semiconductors*, edited by Gibson (Heywood, 1956) appeared in 1956 and is planned to continue as an annual series of critical reviews covering all aspects of semiconductors and to some extent, semiconductor devices. Volume 1 includes articles on: silicon, germanium filament research, the Seebeck effect, electrical properties of phosphors, photo-magneto-electric effect, and field effect in semiconductors.

In Europe, Schottky has continued to edit and publish the papers and discussions presented at the Semiconductor Committee meetings of the Verband Deutscher Physikalischer Gesellschaften. Volumes 1, 2, and 3 of *Halbleiterprobleme* (Vieweg, 1955) contain papers presented at Innsbruck (1953), Hamburg (1954), and Mainz (1955). Volumes in 1957 will include the papers given at the International Colloquium on Semiconductors and Phosphors, Garmisch-Partenkirchen (1956).

In other review series, *Advances in Physics* continues to include solid state topics. Recent investigations on the effects of radiation on solids have been reviewed by Brooks in Volume 6 of *Annual Review of Nuclear Science*; Volume 6 of *Progress in Metal Physics* includes reviews on mosaic structure

and on filamentary growth, while the 19th volume of the *Physical Society Reports on Progress in Physics* gives attention to the infrared absorption in semiconductors.

#### IMPERFECTIONS AND CRYSTAL GROWTH

*Direct observation of dislocations.*—While indirect experimental evidence for the existence of dislocations is extensive and convincing (1), nothing is quite as satisfactory as direct visual observation of dislocations within crystals. Such observations have to a large extent recently proved the reality of dislocation concepts.

Networks in single crystals of AgBr were first studied by Hedges & Mitchell (2), using the photolysis of AgBr to decorate dislocation lines throughout the volume of the crystals with print out silver. Some dislocations were found to occur in rows, others in hexagonal networks dividing the crystal up into cells of  $\sim 10\mu$  diameter. Observation depended critically on annealing treatment; decoration apparently occurred only in strained crystals. Similar results have been obtained by AgCl by Kanzaki (3). Networks in NaCl single crystals were found by Amelinckx (4) in crystals colored with excess sodium. Network nodes were preferentially decorated, and it appeared that screw dislocations could not be revealed at all. Bontinck & Dekeyser (5) made similar network studies in natural  $\text{CaF}_2$ , and van der Vorst & Dekeyser (6) showed that dislocation lines in NaCl treated with silver luminesced.

The observation of single dislocations has been carried out in three different ways. The most direct method was the use of a high-resolution electron microscope [Siemens "Elmiskop," resolution  $\sim 10$  to  $20 \text{ \AA}$  (1)] to observe thin crystals directly; Hirsch, Horne & Whelan (7) studied thin foils of aluminum and found evidence of single dislocation lines, which moved as the sample heated. Movement started with a bowing out of the dislocation line, consistent with the mechanism Mott suggested for the decrease in elastic modulus due to dislocations (8). Menter (9) obtained striking electron photomicrographs of edge dislocations in thin crystals of copper and platinum phthalocyanines. The recent availability of highly perfect silicon crystals made it possible for Bond & Andrus (10) to select a single edge-type dislocation, and by looking at it "end on" in polarized infrared light they observed the stress-induced birefringence. Dash (11) found that copper decoration of dislocation lines running through near-perfect silicon crystals was observable in the infrared, including loop patterns identified as Frank-Read sources.

The study of single dislocations is a subject with many open questions remaining, such as the relation between spiral etch pits and internal dislocation structure [Bardsley & Straughan (12); Dash (11)]. The fact that dislocations can be observed directly in materials opens up an extensive field for the direct study of microscopic mechanical and chemical effects in solids.

*Etch pit studies and techniques.*—The direct observation of dislocation lines

as discussed above is not possible in all materials so one must often resort to indirect methods. The most powerful of these is the observation of surface pits produced by various forms of chemical etching. Conclusive proof that these pits represent the intersection of dislocation lines with the surface under study is given by Dash (11). The decorated dislocation lines, he observed, terminated at etch pits on suitably etched surfaces. Striking work on other materials has been done recently. Gilman & Johnston (13) have been able to produce geometrical pits with structure that identifies screw and edge dislocations in LiF crystals, and using sequential etches they have demonstrated glide of individual dislocations with applied stress and climb upon heating. Billig (14) has reported the use of an alkaline  $K_3Fe(CN)_6$  solution which produces hollow tetrahedral pits with triangular cross section on germanium and silicon rather than the conical type usually produced by "CP4." These depressions have asymmetry which probably denotes obliqueness of the dislocation line to the surface. An interesting variation from the usual "pits" was observed by Allen & Smith (15) who with the aid of a scanning reflection electron microscope observed that etching sometimes produces "humps," i.e., elevations, instead of pits. They speculate that dislocations free from condensed impurities account for the raised features and that pits are usually formed when highly condensed atmospheres exist.

*Crystal growth and whiskers.*—A considerable advance in the understanding of growth kinetics of crystals was made when Frank (16, 17) proposed his theory of crystal growth by a screw dislocation mechanism, according to which new atomic layers are built up by the advancement of a step round and round the dislocation like a spiral ramp. This mechanism does not require the two-dimensional nucleation of an "island" of atoms to achieve rapid growth of crystals at supersaturations far below those required to nucleate new layers. Much evidence supporting this theory has accumulated (18).

An interesting and important facet of this problem is the study of "whiskers." The unusual mechanical properties of these fine filaments, first reported by Comton, Mendizza & Arnold (19) have led to extensive investigations of whiskers from a variety of metals and nonmetals. There is general agreement that the presence of one or more screw dislocations is essential for their growth, a single dislocation running along the axis of the whisker—this being the only imperfection in an otherwise perfect single crystal (20). As a consequence, strengths up to 1000 times that of bulk single crystal specimens are observed (21). The torsional properties of whiskers are being studied at the present time in several laboratories; torsional strain is expected to be present as a result of the screw dislocation running along the whisker axis.

#### LOW TEMPERATURE TOPICS

*Production of low temperatures.*—Probably the most interesting develop-

ment during the last year was the work of Kurti *et al.* (22) who were able to reach magnetic temperatures of  $20 \times 10^{-6}^\circ\text{K.}$  in copper. The method used is the direct adiabatic demagnetization technique to remove nuclear entropy; the heat of magnetization is absorbed by a thermal sink consisting of an electron paramagnetic substance adiabatically demagnetized to about  $0.01^\circ\text{K.}$  (glycerol-chrome potassium alum in this case). At present the aim is largely to understand the interactions of nuclei in solids. For example, one interesting question is the observed rate at which the nuclear spins equilibrate with electrons and lattice [Kittel (23)].

*Superconductivity.*—Superconductivity remains one of the great unsolved problems of solid state physics. On the microscopic level the picture has become somewhat more confused; conversely, recent experimental work has placed the semiempirical energy gap model of superconductivity on a much stronger basis, and encourages the belief that a simple theoretical basis for the phenomenon can be found.<sup>3</sup>

One group of theories centers around the analogies between superfluidity and superconductivity. Blatt, Butler & Schafroth (24) demonstrate that equilibrium superfluidity requires correlation between particle momenta over the entire volume of the containing vessel, and hence an infinite "correlation length." This property belongs only to an ideal boson gas of noninteracting particles. Schafroth (25) shows that superfluidity and superconductivity are equivalent properties of a charged boson gas, and such a gas will satisfy London's equations. Since no real gas possesses an infinite correlation length, London's equation must be modified appropriate to a finite correlation length (26). The connection between the hypothetical charged boson gas and an electron gas remains obscure, although it is suggested the superconducting electron states may in fact be two-particle states involving a spin interaction (27) and will perhaps obey Bose-Einstein statistics.

Recent measurements (28, 29) of the specific heats of superconductors have shown a remarkably precise agreement with the simple formula  $C_{es} = \gamma T_{ca}e^{-bT_c/T}$  where  $C_{es}$  is the electronic specific heat in the superconducting state,  $\gamma$  is the coefficient for the electronic specific heat in the normal state,  $T_c$  is the critical temperature, and  $a$  and  $b$  are constants independent of or only weakly dependent on the specific material. Chester (30) shows that the normal specific heat must persist in the superconducting state strengthening the interpretation of  $C_{es}$  as a quantity of physical significance. Such an exponential law is compatible with an energy-gap model, in which the normal electrons occupy a continuum of levels a discrete distance above the condensed superconducting electrons. The thermodynamic implications of an energy-gap model have been considered by Lewis (31).

Microwave absorption measurements on superconductors have at last become possible in the interesting millimeter wavelength region. Measure-

<sup>3</sup> Since the preparation of this review, a new theory of superconductivity has appeared (257). The theory produces not only the features of an energy gap, but also a penetration depth in essential agreement with the Pippard equation.

ments of surface conductivity (32, 33) in tin and aluminum have shown that the high-frequency resistance breaks sharply from its normal value at temperatures somewhat less than  $T_c$ , this temperature becoming lower with increasing frequency. At the frequencies and temperatures studied, the resistance did not vanish, and at the higher frequencies, extrapolation of the curves would show no vanishing even at absolute zero temperature. The interpretation of these data also suggests an energy gap across which the electrons could be excited into normal states by the microwave energy, the gap increasing as the temperature is lowered (34). More recently, transmission measurements as a function of frequency have been made on a lead film, and these show a strong absorption peak (35). The existence of such a peak again implies an energy gap, and the data are shown to be fitted by assuming a gap of the order of  $3kT_c$  (36).

A further significant advance has occurred with the measurement of a nuclear resonance Knight shift attributable only to the superconducting state (37, 38). Suspensions of colloidal mercury in albumen were used, the small particles permitting field penetration without destruction of the superconducting state. The shift is appreciably smaller in the superconducting state than in the normal state. This implies a marked decrease in the spin-produced magnetic field near the nucleus, either by a destruction of the normal Pauli-type paramagnetism or by a modification of the electronic wave functions near the nucleus.

*Low temperature thermal conductivity of solids.*—In recent years the measurement and interpretation of low temperature thermal conductivity have added much information on defects in solids [Klemens (39)]. Further theoretical attacks were made on the Boltzmann equation (40, 41) in 1956 and measurements were reported on metals (40, 42 to 45), semiconductors (46, 47), graphite (48, 49), liquid helium (50), and dielectric crystals (51, 52, 53).

One defect relevant to thermal conductivity has only recently received attention—naturally occurring isotopes. For many nonmetals, the measured conductivity is not exponential and not as large as theory would have it; an answer in terms of isotope scattering of phonons has now been given by Slack (54) and by Berman, Foster & Ziman (51). The hypothesis that dislocations might be responsible was rejected by Rosenberg after measurements on germanium crystals. Although existing data can be understood by appealing to this isotope effect, ionic crystals with single isotopes should be measured to test the theory further. It may well be that one of the major difficulties in explaining the low-temperature thermal conductivity of nonmetals has now been resolved.

*Lattice vibrations.*—The general subject of lattice vibrations in solids has received continuous attention since the original Born-von Karman and Debye work. Until the last decade attention had been directed largely to simple solids and special topics in the vibration spectrum (55). Largely as a result of heat capacity measurements on anisotropic materials (56) there has been recently revived interest in the subject. Several other related phenomena

have received attention: low temperature thermal conductivity, neutron scattering (57), and electronic and optical properties of semiconductors (58, 59, 60). Major topics in lattice vibration studies are: the choice of force constants in various models, singular properties of the vibration spectra, specific applications—primarily graphite. Several Born-von Karman calculations have been made on the graphite lattice (61), involving one or more approximations: treating the system as purely two dimensional; separating modes into noninteracting "out of plane" and "in plane" displacements; using nearest neighbor interactions only; and fitting a limited number of force constants to data without regard to relations imposed between them by elastic equilibrium conditions. Newell (62) showed that in lamellar crystals the true situation is a combination of both geometric limitations on the vibration spectra (63) with low frequency anomalies in the vibration spectra of systems involving bond bending oscillations. Recent work incorporating these features seems to agree well with experiment (61, 64). In these and other calculations [Harrison (59); Baldock (61)], it has been noted that the relative choice of force constants between next nearest neighbors must obey certain conditions in order that the potential energy be invariant under uniform rotations of the crystal. Such constraints have not always been incorporated into calculations.

Finally, a significant contribution to the theory of frequency distributions and critical points in vibration spectra has been made by Phillips (65). It has been noted by previous authors that singularities of frequency distributions in  $K$  space occurred where the group velocity had zeros. Van Hove classified the nature of these singularities for some cases. The present analysis greatly extends this study using group theoretical and topological methods, and in addition treats behavior near degeneracies. These methods can also apply to electron energy bands.

#### SOLID STATE CONTRIBUTIONS TO CHEMICAL PHYSICS

*Surface studies on semiconductors.*—Past interest in surface phenomena has been associated with catalysis and electrochemistry. Recently the advent of semiconductor devices has presented new problems to those interested in the understanding of surface phenomena. Undesirable variations of device parameters arise from surface effects and the difficulties associated with their control illustrate the lack of fundamental understanding of surface chemistry and physics.

The two semiconductors which have been primarily investigated in recent years are germanium and silicon; these have a potent advantage in purity and understanding of bulk properties over substances which have been studied previously.

Since Bardeen (66) postulated the existence of surface states on semiconductors, many attempts have been made to measure the relative position of these states with regard to the band structure of the bulk material. During the past two years progress has been particularly rapid. Of principal interest



have been: techniques for obtaining clean surfaces (67); the modulation of surface conductance and capacitance by surface electric field induced changes in electron occupation of surface states (68, 69, 70); surface effect induced modification of junction rectifier characteristics (71); surface recombination of electrons and holes—slow surface states (apparently chemically different from bulk) and fast states (identifiable with bulk material) (72).

*Low energy electron diffraction studies.*—Davisson & Germer in observing the diffraction of low energy electrons by a crystal (73) noted the presence of several diffraction beams from an adsorbed gas layer on the face of the crystal. Because of the limited penetration of low energy electrons (74), the diffraction intensity from such an adsorbed layer is generally of the same order of magnitude as the diffraction from the crystal itself. One can in this way determine the exact structure of a monolayer of chemisorbed gas and at least qualitative information on the rate of formation of such a monolayer and the distance between the monolayer and the surface of the crystal (72).

Recently, Farnsworth's group has used this method to evaluate surface cleaning techniques on germanium and titanium. Their results indicate that crystal surfaces producing a diffraction pattern typical of the crystal structure without adsorbed gas can be obtained by a combination of outgassing in high vacuum, bombardment of the surface by positive argon ions, and annealing. The degree of cleaning is, however, dependent on the impurities in the crystal and their rates of diffusion at the annealing temperatures as well as the vacuum and sputtering conditions; in many cases, good results are obtained only by cycling the cleaning process (72).

An example of the application to simple catalytic reactions is the study of hydrogenation of ethylene on nickel and platinum (75). While the method is extremely powerful in achieving graphic analysis of monolayer chemisorption, the major disadvantage is the large amount of time, on the order of six months, necessary to make a detailed study of just one crystal face with present techniques. However, because of the importance of this type of information in the fields of chemisorption and catalysis, it is possible that the method will receive wider use.

*Field emission microscopy.*—The usefulness and versatility of the electron field emission microscope for the studies of metals and metal-adsorbate systems have been greatly extended during the past year. The possibility of seeing individual molecules has received further attention. Although the resolution of a smooth emission tip is insufficient to distinguish individual adsorbate atoms, Rose (76) has substantiated theoretically the suggestion that small protrusions on a metal surface can provide areas with considerably increased magnification and resolution. In an accompanying paper, Becker & Brandes (77) presented photographs of images attributable to single molecules on the surface of emitters prepared under conditions expected to produce the protrusions analyzed by Rose. These molecular images were not obtained for emitters of which the surface had been smoothed by heat treatment.



During the past year, Dyke and his co-workers (78) have reported extensions of the "T-F" technique (studies of electron emission in the combined presence of high temperature and high electric field). The new technique, termed pulsed T-F emission, permits studies of surface reactions at high temperatures with minimum disturbance due to the electric field by applying the field as short pulses. Studies have been made of surface migration and desorption and of the high temperature diffusion of volume impurities to the surface of a tungsten emitter.

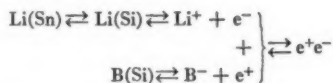
Lewis (79) has shown that the differences observed between the field emission currents measured by Dyke and his co-workers (80) for very high fields and those computed from the Fowler-Nordheim law may arise because of a break-down in the model assumed for the theory. Murphy & Good (81) present the theory of thermionic and field emission from a unified point of view and explore the transition between thermionic and field emission. Experiments of Dyke and his co-workers (80) reach this transition and satisfactory agreement is obtained.

Direct observation of phase changes in titanium, such as described by Brock (82), illustrates another use of the field emission microscope, and, particularly if coupled with the pulsed T-F technique of Dyke, should extend the studies of allotropic transformations in a detail not attainable with conventional methods.

The extreme resolution displayed in the photographs obtained by Müller (83, 84, 85) with the field ion microscope is one of the year's high points. These pictures clearly resolve details at atomic dimensions (2 to 3 Å). The desorption studies of Müller (86), coupled with the suggestion of Inghram & Gomer (87) for use of the field ion microscope as a point ion source for a mass spectrometer, are certainly a very powerful tool for investigations of surface chemistry and physics.

*Association of defects in solids.*—In an extensive paper on solution chemistry, Reiss, Fuller & Morin (88) review their previous work (89, 90) and present a large body of experimental results, as well as an extensive theoretical treatment of the chemical interactions among defects in silicon and germanium. With the availability of these materials in semiconductor-grade perfection, it became possible to test quantitatively the validity of the mass action law where, as originally proposed by Wagner, the electrons, holes, lattice defects, and impurities within a solid are considered as chemical entities in solution.

The composite equilibrium



$\text{e}^-$  denotes electrons

$\text{e}^+$  denotes holes

$\text{Li(Sn)} \rightleftharpoons \text{Li(Si)}$  denotes the distribution equilibrium of lithium between molten tin alloy and silicon.

was considered and the solubilities of lithium in boron-doped silicon found to be governed by the mass action law based on these equations. It is assumed that a lattice vacancy  $\square$  becomes mobile at temperatures above 650°C. so the above equilibrium is superseded by the formation of the complex ion  $\text{LiB}^-$  according to  $\text{Li}^+ + \text{B}^- + \square + e^- \rightleftharpoons \text{LiB}^-$ .

Solids are thus considered a medium for chemical reactions,  $e^+$  being regarded as an analogue of the hydrogen ion,  $e^-$  as that of the hydroxyl ion, while  $e^-e^+$  is a counterpart of water or some other weakly ionized substance. Lithium may then be looked upon as a base while boron is an acid.

Longini & Greene (91) derive expressions for the chemical potentials of donor and acceptor impurities which agree with those of Reiss (92). They then apply the theory to the following phenomena: amphoteric impurities, e.g., copper in germanium; lattice vacancies and diffusion; distribution coefficients of ionizing impurities between two phases; charge balance in insulators; and the connection between crystal growth rate and the resulting nonequilibrium distribution of impurities between the two phases.

#### SEMICONDUCTORS

This was one of the major subjects in last year's review, so the following topics have been selected on the basis of recent developments.

*Optical absorption in germanium and silicon.*—Information on infrared absorption in semiconductors has been somewhat systematized by the publication in 1956 of a broad survey covering germanium, silicon, InSb, and tellurium (93). In current research subsequent to that publication, several highly detailed studies of optical effects in germanium and silicon have been extended to provide further information on impurity and intrinsic absorption and photoconductivity. The optical excitation and ionization energies have been measured with a precision of better than 0.001 eV for Group III acceptors (94) and Group V donors (95). Comparison with thermal activation energies and effective mass theories show improving agreement, but the need for further theoretical refinement is clear. Along these lines, further developments have been reported on the theory of absorption line broadening in silicon (96); and a dependence of these spectra on impurity concentration above  $10^{16}/\text{cm}^3$  has been measured (97). In germanium the study of doubly ionizable impurities is progressing in several laboratories (98). Further data are reported on emission bands at 0.72 eV and 0.53 eV which are attributed to intrinsic (direct) and extrinsic (indirect) recombination respectively (99), and absorption spectrum attributed to interband transitions (100). The study of free carrier absorption and correlation with energy band theory has been reported by Fan on *n*-type germanium (101), and in greater theoretical detail by Kane (102) who has calculated the effects of the known complexities of the energy band structure. Kane's work includes an extensive discussion of perturbation theory, including both spin-orbit and " $k \cdot p$ " terms, for degenerate bands. The absorption by free carriers has been used to determine the

distribution of free carriers in germanium and to measure bulk carrier lifetime without applying electrical contacts to the sample (103). The presence of oxygen in germanium or silicon has been shown to produce absorption bands at  $11.6 \mu$  and  $9 \mu$  respectively (104).

*Semiconductor transport properties (nonquantum case).*—The behavior of semiconductors under the influence of electric fields, magnetic fields, and thermal gradients necessarily depends on the energy band structure (EBS) and the relaxation time  $\tau$  since both appear in the transport integrals which determine current densities. The general features of the many valley band model were reviewed last year. Galvanomagnetic measurements have been most fruitful in investigating various transport theories based on these EBS. In their more hopeful simplified version theories have neglected the dependence of  $\tau$  on direction of electron motion (105, 106, 107). Herring & Vogt (108) developed a transport theory in which the anisotropy of  $\tau$  as well as the EBS is taken into account for ellipsoidal energy surfaces. They show that for static fields, the transport properties always have the reciprocal of each effective mass (in the principal axis system) weighted by the  $\tau$  in the corresponding direction. Thus, rather than  $K$ , the reciprocal effective mass ratio, one actually measures  $(\tau_{\perp}/\tau_{\parallel})K$  where  $\tau_{\perp}$  and  $\tau_{\parallel}$  are the relaxation times respectively perpendicular to and parallel to the principal axis directions.

McClure (109) has shown that the components of the magnetoconductivity integrand can be written in the form of a Fourier series expansion in  $[1 + (n\omega\tau)^2]$  for a broad category of EBS where  $\omega$  is the cyclotron resonance frequency; only the first harmonic appears in the case of ellipsoidal energy surfaces.

Goldberg & Davis (110) used weak field ( $H \rightarrow 0$ ) measurements of magnetoresistance in  $n$ -germanium to determine  $K$  and  $\tau$  vs. temperature from 80°K. to 300°K. They obtained a mass ratio of about 12 and an apparent temperature variation of  $\tau$ . They considered it likely that the discrepancy between their value of  $K$  and the cyclotron resonance value ( $K$  about 20) was due to anisotropy of  $\tau$ .

Broudy & Venables (111) reported a technique for obtaining magnetoconductivity components for direct comparison with theory. Their method was applied to  $n$ -silicon and  $n$ -germanium whose  $(\tau_{\perp}/\tau_{\parallel})K$  was found to be about 20 above 120°K. and decreased at lower temperatures. This result is in agreement with the cyclotron resonance value and with the theory of Herring & Vogt (108) in that  $(\tau_{\perp}/\tau_{\parallel}) \approx 1$  in the lattice scattering region but decreases in the impurity scattering region. Goldberg (112) was able to determine directly the transverse component of the magnetoconductivity tensor by applying low resistance electrodes to the faces of a large area thin plate of  $n$ -germanium. His results for  $(\tau_{\perp}/\tau_{\parallel})K$  in this experiment are in agreement with those of Broudy & Venables.

Theoretical calculation of  $\tau$  and related mobility has received attention. Mobility in semiconductors is limited by the following scattering mecha-

nisms: "Lattice scattering," by the thermal vibrations of the lattice; ionized impurities; neutral impurity atoms; miscellaneous stationary defects, such as boundaries, neutral dislocations, etc.

The basic and straight forward approach to lattice scattering was pioneered by Bloch & Nordheim (113). Bardeen & Shockley (114) developed the somewhat more artificial deformation potential formalism. In 1956, Dumke (115) extended deformation potential theory to the many-valley type band structure found recently in *n*-type germanium, and he found that transverse or shear modes of vibration contribute to lattice scattering, in fact dominantly so. Deformation potential mobility has a temperature dependence of  $\mu_L \sim T^{-1.5}$ . Experimental results are  $T^{-1.66}$  and  $T^{-2.3}$  for *n*- and *p*-type germanium, respectively, and  $T^{-2.5}$  and  $T^{-2.3}$  for *n*- and *p*-type silicon (theoretical papers referred to contain references to experiments). In a series of two papers Ehrenreich & Overhauser (60) developed the Bloch & Nordheim approach to the special case of the band structure found in *p*-type germanium. Using a proper admixture of optical and acoustical mode scattering, their theory is developed to within a few arbitrary parameters which are fitted to experimental data. Harrison (59) also finds that experimental data for *p*-type germanium, as well as *n*-type germanium and *p*-type silicon, can be fitted by mixing the right amounts of optical and acoustical mode scattering. Previous theories of ionized impurity scattering (116) were based on classical formulas and on the Born approximation for scattering by screened coulomb potentials. Sclar (117) and Blatt (118) simultaneously presented a new approach, based on the method of partial waves for calculating scattering cross sections. In the limit of long carrier wavelength (low temperatures) and short range scattering potentials, the new theories lead to much higher mobilities and different temperature dependence.

Herring & Geballe (119), Steele (120), and Willardson & Beer (121) investigated thermomagnetic effects (Nernst, magneto-Seebeck, and magnetothermoelectric power) including the "phonon-drag" effect. Sondheimer (122) gave a general proof of the validity of the Kelvin relations for thermoelectric effects. ter Haar & Neaves (41) derived equations for the theory of thermoelectric power and thermal conductivity consistent with the Kelvin relations. Price (123, 124) has presented a development of thermoelectric and thermomagnetic effects from a phenomenological point of view.

*Experiments in high magnetic fields (quantum effects).*—Historically, the modern understanding of transport problems in semiconductors and metals traces to the work of Lorentz (125) and Sommerfeld (126). These initial treatments have been extended by many authors with various degrees of generality, usually in limiting cases of either very weak or very strong magnetic fields (109). Recently several authors (107, 109, 127 to 133) have considered this problem with emphasis on transport properties at intense magnetic fields and with varying assumptions of more general band structures. The direct stimulus for this has been increased availability of high field pulsed magnets.

The most important consequence of an intense magnetic field is that the quantized orbits of the carriers (electrons, holes) become important. As expected at high fields, the relaxation time  $\tau$  may be dependent on the magnetic field strength. Consequently, the predictions of the ordinary Boltzmann equations must be re-examined carefully. Recently extremely interesting measurements of the longitudinal magnetoresistance of germanium have been made at pulsed fields as large as 600 kilogauss (134) and of the magnetoresistance of copper, tin, and aluminum at fields as large as 200 kilogauss (135). Also, two other experiments have been reported during the past year which promise to provide additional information about the diamagnetic energy levels in semiconductors. The shift in the infrared absorption edge due to an applied magnetic field (136, 137, 138) has been observed in both InSb and InAs. In these materials the splitting of conduction band levels in a magnetic field is relatively large due to the small effective mass of the electrons (138). The quantization of levels at the band edge shifts the effective optical band gap producing a change in the absorption edge with magnetic field.

A related experiment utilizing thermal rather than optical energies has also been reported (139, 140). This consisted of measuring the d.c. conductivity and Hall coefficient of InSb as a function of temperature and magnetic field strength. A plot of this data, showing the effective number of carriers vs. magnetic field for various temperatures, provides a method of studying the ionization energy in InSb for transitions between the donor levels and various diamagnetic levels in the conduction band. The change in ionization levels for hydrogen-like wave functions in a strong magnetic field has been studied with regard to this problem by Yafet *et al.* (141).

These various high field measurements are very new, but it is already clear that they will soon be of major interest in the field.

*Transport properties of semimetals (graphite, bismuth).*—Graphite is semimetallic in the basal plane, has extreme anisotropy of transport properties, and exhibits striking magnetic field dependence of electrical and magnetic properties (142 to 145). Recently work carried out on superior natural single crystals at low magnetic fields ( $H \geq 16$  gauss) gives the first experimental evidence of very light current carriers (very light holes and possibly light electrons) (146). A general treatment of the magnetoconductivity tensor for the case of arbitrary band structure and magnetic field where parameters are determined from the experimental galvanomagnetic data has been recently developed (109) and applied to the results for graphite. Cyclotron resonance work (147, 148) yields values of  $0.05 m_0$  and  $0.07 m_0$  for the majority electrons and holes, respectively, and  $0.015 m_0$  and  $0.028 m_0$  for the minority electrons and holes, respectively, which corroborate those values obtained from the static measurements above.

Bismuth has been investigated more extensively than graphite. Its extremely large magnetoresistivity (149) is the highest of any material known. Interpretation of the galvanomagnetic measurements of bismuth has also been made with the conclusion that the two bands slightly overlap

by  $\sim 0.012$  eV (105). Cyclotron resonances have been observed in bismuth (150, 151) giving values of  $0.3 m_0$  and  $0.0015 m_0$  for two of the effective masses corresponding to the values found from the de Haas-van Alphen measurements. Miscellaneous studies have also been made on the transport properties of bismuth with parameters of pressure (152, 153) and impurity doping (154).

These investigations are typical of an expanding interest in anisotropic materials, where the asymmetry emphasizes points not clearly recognized in simpler solids.

*Miscellaneous developments in intermetallic compounds.*—Mooser & Pearson (155) proposed that the concept of a specific "semiconducting bond" could be used to describe semiconducting compounds. They assert that atoms from Groups IV to VII are necessary for the formation of such essentially covalent bonds. If  $n_v$  is the number of valence electrons per molecule,  $n_a$  the number of Group IV to VII atoms per molecule, and  $b$  the average number of bonds formed by one of these atoms with other Group IV to VII atoms, then the condition for the bonds to be semiconducting is  $n_v/n_a + b = 8$ . All known semiconductors, except perhaps for boron, its compounds, and some hydrides, may be described in terms of such bonds. The presence of empty "metallic" orbitals in some atoms (such as should exist in CdSb) does not destroy semiconductivity provided that these atoms are not bonded together. The advantages of the chemical valence scheme over simple band theory are that it may be applied to compounds containing transition elements, it does not require a precise specification of the crystal lattice, and it may be applicable to semiconducting liquids.

The magnetic susceptibility as a function of temperature has now been measured (156) for all Group IV semiconductors and III to V intermetallic compounds. All of these materials are diamagnetic with minimum diamagnetism at some critical temperature below which the susceptibilities are about what would be expected from closed shells and paired valence electrons and above which the magnitude increases from one material to the next nearly linearly with the average number of electrons per atom. Notable exceptions are silicon, germanium, and GaSb which have surprisingly small susceptibilities. Up to the critical temperature the diamagnetism decreases linearly, but slowly, as the temperature increases. This may be accounted for by the "Van Vleck paramagnetism" of the valence electrons as suggested by Krumhansl & Brooks (157).

#### RESONANCE METHODS

*Electron, nuclear, and cyclotron magnetic resonance.*—A number of new electron resonance observations of impurity states have been reported. Work on color centers in halides is reviewed in a following section; hyperfine structure has been resolved and new centers have been studied. Feher and co-workers (158) have observed weak satellites situated between the hyperfine components in the electron spin resonance in phosphorus doped silicon;

exchange coupling between two or more electrons acting as a unit could interact with the P nuclear spin and give rise to the additional lines. In the purest samples, relaxation times as long as one minute were observed at liquid helium temperatures (159). Other interesting electron spin resonance experiments deal with hydrogen atoms "frozen out" at liquid helium temperatures (160), and surface effects associated with the resonance in charred materials (161, 162, 163).

Experiments on metals include the measurement of the paramagnetic contribution to the magnetic susceptibility of conduction electrons in lithium and sodium (164) by comparing the electron spin resonance intensity with the nuclear spin resonance intensity in the same sample under identical experimental conditions. The nuclear susceptibility was calculated using the Langevin-Debye formula; results for the electron paramagnetic susceptibility were in agreement with the theory of Pines and Bohm. Knight and co-workers (165) have measured both the nuclear and electron spin resonance in dilute alloys of manganese in copper. Both the nuclear and electronic Knight shifts were much smaller than expected from interactions between the *d*-electrons of the manganese and the conduction electrons. The line width of the copper nuclear resonance was larger in the alloy than in pure copper. Bloembergen and co-workers (166) measured the Knight shift in the nuclear resonance of sodium as a function of pressure. From the results, the electron probability density at a sodium nucleus was estimated and found to be in agreement with other estimates. A highlight of the year was the observation of nuclear resonance in a superconductor, by Reif (37) and by Knight (38), discussed under *Superconductivity*.

Cyclotron resonance experiments have now been extended to much higher frequencies—notably to the infrared region [discussed partially under *Experiments in high magnetic fields* (138, 167, 168); also *Superconductivity*]. Cowan & Gordy (169) have extended the microwave electronic methods to obtain wavelengths as short as 0.587 mm. There are two main motivations for measuring cyclotron resonances at higher frequencies. First, resonances can be observed when relaxation times are shorter, allowing a greater variety of materials and temperature conditions. Second, the variation of the measured effective masses with magnetic field provides a means of studying the detailed shape of energy bands. Work in the microwave region continues. Recent studies at these frequencies have concentrated on metals and semi-metals such as bismuth (150, 151), tin, copper (170), and graphite (147). The interpretation of these results has been complicated by the anomalous skin depth effect which occurs in metals when the condition for cyclotron resonance is satisfied. This problem is now receiving considerable attention (171 to 175). To the present date, however, neither the theory nor the experiments are in a state which allows definite interpretation.

*New resonance methods and applications in solids.*—Recently, double resonance techniques have become an important addition to the standard magnetic resonance experiment. Samples are excited at two different fre-



quencies simultaneously, altering the population of a multilevel system. Pound (176) enhanced the nuclear resonance absorption of sodium in  $\text{NaNO}_3$  by simultaneously imposing R.F. frequency corresponding to quadruple splitting of the sodium levels. Overhauser (177) proposed a method of polarizing nuclei in metals by saturating the conduction electron spin resonance; this was observed in a double resonance experiment by Carver & Slichter (178). Similar effects have been observed for free radicals (179).

Feher (180) has recently proposed a scheme for nuclear polarization using the rapid passage technique on systems in which the hyperfine structure is resolved and the predominant nuclear relaxation process involves an  $\vec{I} \cdot \vec{S}$  type hyperfine interaction. The induced population differences were observed in the phosphorous nuclear resonance in silicon. This technique requires that a certain fraction of the external magnetic field is swept in a time less than both the electron and nuclear relaxation times. The double resonance technique can be used to determine nuclear hyperfine interactions and  $g$ -values (181). The R.F. frequencies allow a direct measure of both. Herzog & Hahn (182) have described effects on the transient nuclear induction signals in solids containing different nuclei—phenomena similar to the high-resolution, double-resonance experiments on liquids reported by Bloom & Shoolery (183). Bloom points to one essential difference between these and the Overhauser effects, namely, that the primary thermal relaxation process for nuclei in the Overhauser effect must be through the nuclear-electron spin coupling, not for the Bloom and Hahn experiments. There will undoubtedly be many more applications of the double resonance technique to systems in which the interpretation of results of single resonance experiments are ambiguous or not very detailed.

An extremely important development is the solid state Maser. Townes and co-workers (184, 185) first described an apparatus which could be used as a microwave spectrometer, a microwave amplifier, or as an oscillator using a molecular beam. This apparatus was named the Maser which stands for "microwave amplification by stimulated emission of radiation." Such systems potentially have extremely low noise.

Bloembergen (186) has recently proposed a solid state Maser utilizing the electron spin levels in paramagnetic systems. This method involves saturating one transition of a multiple energy level system in order to alter the population difference of some other pair of levels. Amplification can then be obtained by stimulating the emission between this latter pair of levels. Combrisson, Honig & Townes (187) have reported power amplification using a rapid passage technique on the electron spin levels of phosphorous-doped silicon. The total emission of these samples was only slightly less than would be required to sustain oscillations in the resonant cavity. Improvement of solid state Maser operation depends to a large extent on finding suitable materials, those with high spin concentrations, long relaxation times, sharp resonance lines, and relatively few spin levels. In the multilevel satura-



tion method, the design of satisfactory dual-mode resonant cavities may be a major problem.

#### NONMETALS—OPTICAL PROPERTIES

*Excitons.*—A basic concept of light absorption in nonconducting crystals is the "exciton." Several points of view on its nature have been emphasized in different treatments, but all of these have the common concept of an electronic excitation (usually induced optically) being transferable through the crystal as a consequence of the periodicity degeneracy in a solid. The extreme limits in approximation are represented by atomic excitation wave functions or by Bloch (band) functions respectively as representations. In the former case the transfer of excitation occurs largely via near zone dipole interactions (188); in the latter case the transfer can be considered as the motion of the mass center of the two body system comprising the excited electron and the hole thereby left in a filled band. During the past year Overhauser (189) has made a careful analysis of the spin-orbit produced exciton fine structure at  $K=0$  (appropriate to optical absorption) for cubic structures of the alkali halide type. Using atomic functions and group theory the selection rules allow five or six components in the fundamental absorption edge fine structure of NaCl and CsCl type crystals respectively. Dresselhaus (190) has discussed the other limiting case, extending the Bloch or effective mass approach to degenerate systems. He discusses the validity of the approximation, effects of ellipsoidal band shapes, probable location of exciton absorption in germanium and silicon, and more recently shows that the absorption coefficient is weak for weak binding of the exciton—pertinent to the relatively weak exciton absorption in  $\text{Cu}_2\text{O}$  (191). Miscellaneous related topics of interest are: Inchauspe's (192) observations of exciton induced photoconductivity; Taft & Philipp (193) have observed direct photoelectric emission from the valence band of alkali halides (in contrast to previously identified exciton induced emission); while strong luminescence near the fundamental absorption edge has been reported, it is still not certain that this is due to exciton recombinations (189).

*Photoconductivity, luminescence in ZnS type crystals.*—The 48 papers concerning ZnS type phosphors which were presented at Paris (194) constitute about half the extensive literature appearing during 1956 on the photoconductive, luminescent, and electroluminescent properties of ZnS crystals.

The observation by Prener & Williams (195) that no increase occurs in the green emission band of  $\text{Zn}^{65}\text{S}:\text{Cu}$ , Cl as lattice atoms of  $\text{Zn}^{65}$  decay into  $\text{Cu}^{65}$  has been interpreted in two ways. Using a covalent model, Prener and Williams concluded that an isolated substitutional  $\text{Cu}^+$  activator in ZnS cannot act as a luminescent center, but requires an associated substitutional coactivator as second or third nearest neighbor. However, Schulman & Klick (196) pointed out that using a purely ionic model for ZnS, no additional green luminescence would be expected to occur if the copper were incorpo-

rated as  $\text{Cu}^{++}$ . Thus, while the interpretation of this experiment is ambiguous, it is at least not necessary to modify the usual crystal phosphor model (197).

Evidence for the existence of excitons in CdS has been presented by Grillot (194). The question whether low-temperature edge emission of CdS is caused by exciton recombination has been considered; Lambe, Klick & Dexter (198) conclude it is probably recombination of a free hole with an electron trapped at some lattice imperfection.

Free hole motion in CdS has been demonstrated by the existence of a PME effect (199), as well as by optical scanning experiments with and without additional infrared irradiation (200). Interesting observations on excitation diffusion in sulfide crystals (distances of millimeters) have been made by Balkanski & Broser (201).

Over the past few years, one special topic of interest in luminescence theory has been the semiquantitative discussion from first principles of the emission and absorption spectra of a typical activator. Williams (202) has focused attention on thallium activated potassium chloride. Recently Knox & Dexter (203) have noted the inadequacy of previous discussions in explaining observed oscillator strengths; this has led Williams & Johnson (204) to improve the analysis, noting that in order of perturbation magnitude the crystalline interactions exceed spin orbit effects, and using observed crystalline absorption spectral energies rather than free ion energies.

*Color centers.*—The great variety of optical absorption bands observed in alkali halides continues to be a fertile proving ground for testing models of color centers and other ideas on the nature of these crystals (205). Measurement of the F absorption band in several alkali halides and interpretation of the results in terms of configuration coordinate curves present a possible explanation for the low efficiency of F-center luminescence (206). Measurements of the intensity ratio of the  $R_1$  and  $R_2$  bands in KCl crystals as a function of F light irradiation time (207) show this ratio to be substantially constant. This constancy is interpreted to indicate that both bands originate from a single type center—a finding which is consistent with the Seitz model for an R-center. An experiment (208) in which the low temperature thermal stability of the  $\alpha$ -center is correlated with the associated F-centers further delineates the accepted behavior pattern of F-centers. Luminescence from F-, M-, and R-centers when excited with polarized light has been studied (209, 210). The experimental results are compared with the emission expected from the symmetry properties of the models used. One interesting speculation arising from this work is that perhaps there are excited states of M- and R-centers lying immediately under the F-band. From magnetic resonance data, the F-band oscillator strengths in KCl and NaCl (211) have been determined. The F-center spin resonance in NaF and LiF has been resolved into a series of uniformly spaced lines and the g-factor for the F-center determined (212). Magnetic resonance has been applied to investigation of U-centers in KCl to show the presence of interstitial hydrogen atoms and hydride ions in the lattice as a result of conversion of U-centers to F-centers

(213). Hyperfine splitting of V-centers has been observed by resonance techniques (214). The splitting has been interpreted to be caused by a  $V_2$ -center and extreme localization of the bound hole is indicated (215), or by Känzig as a diatomic negative halogen molecule ion along a 110 direction. Further resonance measurements are being carried out and it is likely that double resonance methods will yield interesting new information.

#### SELECTED MISCELLANEOUS TOPICS

*Diffusion.*—Diffusion measurements of silver in silver chloride by Compton (216) have shown a failure of the Einstein-Nernst (217) relation. The diffusion coefficient calculated from the ionic conductivity was 1.7 times larger than the measured tracer diffusion coefficient. Tubandt (218) was able to show that the chloride ion is not mobile enough to contribute to this failure. McCombie & Lidiard (219) point out that a higher diffusion coefficient is to be expected from the conductivity, if the interstitialcy mechanism of Koch & Wagner (220), as described by Seitz (221), or the correlation effect for vacancy diffusion of Bardeen & Herring (222) are active. In the first mechanism an interstitial ion moves by pushing a neighbor lattice ion into an interstitial site. If the interstitial sites and the lattice position are collinear as Hove (223) shows, the charge would move a distance  $2d$  while the ions move a distance  $d$ .

The structure dependence of diffusion in germanium and silicon has been emphasized by several workers. Tweet & Gallagher (224) have shown that the penetration of copper into crystals with many low angle grain boundaries is a factor of 50 greater than the penetration in relatively perfect crystals at 710°C. Similar effects have been noted by Dash (11) in silicon. Explanation of these effects by Frank & Turnbull (225) points the role of vacancies since exchange is required between the interstitial sites of high diffusivity and the lattice sites for high solubility. A generous supply of vacancies is required for precipitation in the region of the dislocations.

*Gruneisen and Lindemann laws.*—Gilvarry (226) has written a number of papers on the Gruneisen and Lindemann laws and the fusion curves of solids at normal and high pressures. He discusses the relations between a generalized Lindemann law, the order-disorder model of Lennard-Jones and Devonshire, and the Simon fusion equation. It appears that the Lindemann relation is a very good approximation along the fusion curve. One of the interesting results (227) is the clarification of the discrepancy found by Dugdale & MacDonald (228) between the Gruneisen constant,  $\gamma$ , as derived by them for an ideal harmonic body and that derived by Lorentz & Slater (229) for a Debye solid. The former authors were tacitly using an anharmonic model of independently vibrating pairs rather than coupled oscillators as in the Debye theory, so that it is quite understandable how the value of  $\gamma = \frac{1}{2}$  was obtained when one would expect a zero result for the harmonic case. Inclusion of finite strain does not affect the Gruneisen parameter derived for the Debye solid.

*Diamagnetic susceptibility.*—Several interesting developments have taken

place in the theory of diamagnetic susceptibility of solids. The complete theory of the de Haas-van Alphen effect for general band structures has been given by Lifshitz & Kosevich (230), who show how the band structure can be deduced from the experimental data. The theory of the de Haas-van Alphen effect in alloys has been given by Heine, who makes use of the results of Lifshitz & Kosevich (231) mentioned above, and of the work of Friedel (232) on the electronic structure of solid solutions. Chambers (233) gives a review of such methods for band structure examination.

A number of authors have considered deviations from, and corrections to, the Landau-Peierls formula for the diamagnetic susceptibility of conduction electrons. Recent accurate measurements of the magnetic susceptibility of sodium by Bowers (234), when combined with the resonance measurements the spin susceptibility by Slichter & Schumacher (164), lead to a diamagnetism of the conduction electrons smaller than predicted by the Landau-Peierls formula. Kjeldas & Kohn (235) have made a calculation, based on the method of Luttinger & Kohn (236), which takes into account effects neglected by the Landau-Peierls formula. They find, however, that the corrections are small for sodium, though appreciable for lithium. Appel (237) has shown that the magnitude of the Landau-Peierls susceptibility can be reduced by invoking an anisotropic Fermi surface, and proposes this to explain the discrepancy for sodium.

Krumhansl & Brooks (157) have pointed out that the weak temperature dependence of the susceptibility of germanium can be explained on the basis of Van Vleck paramagnetism. The result can also be derived by the Luttinger-Kohn (236) method. The large diamagnetism of graphite has been explained by McClure (238) as the result of transitions between degenerate bands, induced by the magnetic field. It is for just such a case that Adams (239) predicted the deviations from the Landau-Peierls formula could be large.

*Radiation damage.*—Radiation damage in solids has grown in the past ten years from the category of a nuisance in reactor technology to a fundamental research tool for investigating the role of lattice defects in solid state phenomena. The number of review articles on the subject are numerous; some of the more comprehensive recent ones are Brooks (240), Seitz & Koehler (241), and Kinchin & Pease (242). The reader is referred to these for a comprehensive bibliography and a more extended review of the field.

In order to account for some of the results of radiation damage in germanium and silicon, James & Lark-Horovitz (243) proposed a semiquantitative theory in which both vacancies and interstitials are assumed to be doubly ionized, interstitials being donors, and vacancies acceptors. This model has been used to advantage for neutron bombarded germanium, silicon, InSb, and GaSb. Recently Cleland *et al.* (244) have bombarded germanium with gamma rays from a  $\text{Co}^{60}$  source; this type of irradiation, in contrast to neutron and charged particle irradiation, produces randomly distributed Frenkel defects throughout the volume of a sample. Loferski & Rappaport

(245, 246) have redetermined the energy necessary to displace an atom from a lattice site in both germanium and silicon. They found an energy of 12.9 ev to be compared with Klontz (247) who determined a threshold of 31 ev. The discrepancy remains to be resolved.

Radiation damage has been extensively studied in copper, gold, and silver for bombardment at liquid helium temperature. Interesting recent work has been done by Blewitt and collaborators (248). The release of stored energy as well as the resistivity changes on annealing have been measured after neutron bombardment at 18°K. It has been shown that the low-temperature resistivity annealing from 30°K. to 60°K. occurs with negligible stored energy release, ruling out hypotheses that the annealing in this region is due to the recombination of close Frenkel pairs. In these metals annealing from 30°K. to 240°K. occurs without a discrete activation energy.

*Magnetic and dielectric materials.*—Considerable emphasis to date has been expended on oxide based ferrites, partly for practical and also for intrinsic reasons. Recent studies include the sulfide based spinels [Lotgering (249)], which are noteworthy in view of the different chemical bonding. Additional verification of the general mechanism of super exchange was provided by observations of ferrimagnetic behavior in garnet type structures by Pauthenet *et al.* (250, 251). Magnetic interactions in these materials involve three fundamentally different sublattices instead of the two found in ferrites with the possibility of higher saturation values than have been achieved to date. The orthoferrites and cyanides are also receiving some attention (252). Rather significant saturation values have been derived for the cyanides at very low temperatures, whereas the orthoferrites are less consistent in their behavior.

Interesting work has been done by Bean & Jacobs (253), on very small particles of (metallic) magnetic materials. In addition to being of some considerable practical interest, these materials are ideal for basic studies.

Several new isomorphs have been reported of the new class of ferroelectrics represented by guanidine aluminum sulfate hexahydrate (254). Together with the observed ferroelectricity of some alums (255), and the known dielectric anomalies of ammonium sulfate, these have prompted Matthias (256) to propose a prominent role of the N—H—O bond in the production of ferroelectric behavior. The titanates, however, still draw the most attention.

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# NUCLEAR AND ELECTRON MAGNETIC RESONANCE<sup>1,2</sup>

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*Introduction.*—This review covers certain recent developments in the chemistry and physics of magnetic resonance spectroscopy. This field is already much too large to attempt a comprehensive review in the space available here; understandably therefore the review, to some extent, reflects the particular interests of the author. Special attention has been given to those developments in the physics of the subject which appear to be important and promising for chemical applications, and less attention has been given to more or less straightforward chemical applications of well-established techniques. Finally, if a review of this sort is to be of much value it must be timely; this has prompted the otherwise regrettable inclusion of brief references to articles which are doomed to be "in press" for extended periods of time.

*Books and reviews.*—Ramsey (1) has written an excellent and most interesting book on molecular beams which contains a wealth of information on nuclear electric and magnetic interactions in molecules. Many of these interactions are of importance in chemical applications of MR (magnetic resonance).

*Dynamics of MR, including relaxation.*—Adequate solutions to many dynamical problems in MR can be obtained by employing the original macroscopic phenomenological equations of Bloch (2), and the perturbation method of Bloembergen, Purcell & Pound (3) with, perhaps, some elaboration on both developments. Recent work tends to emphasize the fact, however, that the dynamical problem of electron and nuclear magnetic resonance (EMR and NMR) is basically an involved problem in nonequilibrium quantum statistical mechanics. In the most general case one must consider all the magnetic nuclei in a macroscopic sample, in their interactions with one another, with their molecular environment, and with externally applied stationary and oscillatory magnetic fields. The complete dynamical behavior of an ensemble of such macroscopic systems is conveniently described in terms of the density matrix  $\rho$  which refers to both spin and spacial molecular quantum states, and which follows in its time dependence the equation,

$$i\hbar\dot{\rho} = \mathcal{H}\rho - \rho\mathcal{H} \quad 1.$$

$$\mathcal{H} = \mathcal{H}_B + \mathcal{H}_C + \mathcal{H}_D(I) + \mathcal{H}_{II} + \mathcal{H}_L + \mathcal{H}_a \quad 2.$$

<sup>1</sup> The literature survey for this review was concluded in December, 1956. The December 15 issue of *Physical Review* was received too late to be included in this review.

<sup>2</sup> Contribution No. 2177 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology.

$\mathcal{H}_B$ ,  $\mathcal{H}_C$ , and  $\mathcal{H}_D(t)$  are Hamiltonians for the magnetic coupling between the spins and the externally applied stationary field ( $\mathcal{H}_B$ ), time-averaged molecular electronic paramagnetic, diamagnetic or second-order paramagnetic nuclear shielding fields ( $\mathcal{H}_C$ ), and externally applied oscillatory fields which depend explicitly on the time ( $\mathcal{H}_D(t)$ ).  $\mathcal{H}_{II}$  is the time-averaged tensor coupling between spins, including dipolar and exchange type coupling.  $\mathcal{H}_L$  is the lattice Hamiltonian, and  $\mathcal{H}_G$  gives those terms which couple spin and lattice motions and which lead to  $T_1$  spin relaxation. Typically,  $\mathcal{H}_G$  includes magnetic dipole and electric quadrupole interactions.

By extending the earlier work of Wangness & Bloch (4), the latter author has developed a remarkably general and useful quantum statistical treatment of this problem which is particularly applicable to liquids and gases showing NMR fine structure (5). In this work a linear Boltzmann equation is developed for the spin density matrix  $\sigma$  for the magnetic nuclei contained in one molecule under the assumption that the molecular lattice is always in thermal equilibrium.<sup>3</sup>

$$\dot{\sigma}^* + i(E_1\sigma - \sigma E_1) = \Gamma(\sigma_1^*) \quad 3.$$

In equation 3,  $\hbar E_1$  is some small part of the total spin energy,  $\mathcal{H}_B + \mathcal{H}_C + \mathcal{H}_D + \mathcal{H}_{II}$  and generally includes  $\mathcal{H}_D(t)$ ; the representation of  $\sigma$  is diagonal in  $E_0$ , where

$$\hbar E_1 + \hbar E_0 = \mathcal{H}_B + \mathcal{H}_C + \mathcal{H}_D(t) + \mathcal{H}_{II} \quad 4.$$

$\Gamma(\sigma^*)$  is a relaxation frequency matrix involving Boltzmann temperature factors, and is linear in  $\sigma^*$  and quadratic in  $\mathcal{H}_G$ . The elements of  $\Gamma$  are of order  $T_1^{-1}$ ,  $T_2^{-1}$ . In addition to the assumed thermal equilibrium of the lattice, there are certain additional limitations on the validity and form of equation 3 which are

$$(\omega^*, \hbar T/\hbar) \gg (|\Gamma|, |E_1|) \quad 5.$$

$$|(E_0)_i - (E_0)_j| \gg |\Gamma|, |E_1| \quad 6.$$

$$\text{or } 0$$

$$|(E_0)_i - (E_0)_j + (E_0)_k - (E_0)_l| \gg (|\Gamma|, |E_1|) \quad 7.$$

$$\text{or } 0$$

Here  $(\omega^*)^{-1}$  is the effective correlation time for the molecular lattice, and the single and double differences in equations 6 and 7 refer to differences in the eigenvalues of  $E_0$ . When  $\sigma$  is restricted to include only a small number of spins, as in a simple molecular spin system, then the above limitations on the validity of equation 3—especially in regard to the relative values of  $|\Gamma|$  and  $\omega^*$ , and the thermal equilibrium of the lattice—may exclude from consideration systems of high viscosity and spin density, as is frequently the case for crystals.

Bloch (5) has investigated solutions of equation 3 for a number of special cases: (a) When  $\hbar E_1 = \mathcal{H}_D(t) = 0$ , equation 3 yields the ordinary Boltzmann population distribution among spin states. (b) The development of equation

<sup>3</sup> The spin density matrix  $\sigma^*$  differs from  $\sigma$  by a simple unitary transformation.

3 for  $\hbar E_1 = \mathcal{H}_D(t)$  (single monochromatic oscillatory field), and for no degeneracy in the eigenvalues of  $E_0$ , gives a quantitative formulation of the "general Overhauser effect." The problem of evaluating the diagonal elements of  $\sigma$ , the spin state populations, is shown to be equivalent to a d.c. circuit problem, where the resistances are related to spin relaxation rates, and voltages are related through Boltzmann factors to spin state populations. (c) When it is possible to take  $\hbar E_0 = \mathcal{H}_B + \mathcal{H}_C + \mathcal{H}_{II}$ , and  $\hbar E_1 = \mathcal{H}_D(t)$  (such that conditions 6 and 7 are satisfied), then a general formula can be given for the spin resonance line shape, and matrix elements of  $\Gamma$  can be identified with  $T_1$  and  $T_2$  for each signal in a multiplet spectrum. Furthermore, in the absence of saturation (low  $\mathcal{H}_D(t)$  or  $H_1$ ), the integrated line intensities are independent of relaxation effects, and are proportional to the usual spin raising or lowering matrix elements, an assumption implicit in many chemical structural applications of high resolution NMR spectroscopy. Although  $\mathcal{H}_{II}$  for molecular spin systems in liquids is bilinear in the spins and isotropic and does not of itself give rise to spin relaxation, the relaxation times for one spin in a molecule can be directly affected by the relaxation times for another spin through the isotropic spin-spin coupling. Bloch gives a quantitative discussion of this effect for the case of two nuclei of spin  $\frac{1}{2}$ , with arbitrary ratio between spin coupling and chemical shift, and with external dipolar relaxation.  $T_1$  and  $T_2$  for each of the four multiplet signals are expressed in terms of the spin coupling-chemical shift ratio, and the four possible relaxation times for the uncoupled nuclei. In this connection it is significant that  $T_2$  for any one of the four multiplet signals depends on the uncoupled  $T_1$  for the other spins. (d) For  $\hbar E_0 = \mathcal{H}_B + \mathcal{H}_C$  and  $\hbar E_1 = \mathcal{H}_{II} + \mathcal{H}_D(t)$ , Bloch considers the effects on multiplet line shapes and splittings of strong, intermediate, and weak relaxation,  $\hbar|\Gamma| \gg, \sim, \ll |\mathcal{H}_{II}|$ . Quantitative line-shape formulas are developed for the case of two spin-spin coupled nuclei, with different relaxation times due to external dipole relaxation. The formulas display the well-known collapse of multiplet pattern when the relaxation frequency of one of the spins exceeds the multiplet splitting. (e) Also under the condition that  $\hbar E_0 = \mathcal{H}_B + \mathcal{H}_C$  and  $\hbar E_1 = \mathcal{H}_{II} + \mathcal{H}_D(t)$ , Bloch develops the theory of the double resonance experiment. A quantitative theory of resonance line shapes found with a weak rf field is developed for the condition that the nuclear system is simultaneously exposed to an intense rf field of different frequency. Characteristic double resonance effects are expected even if the sample contains equivalent nuclei, and these effects can be used to calibrate the rf field intensity in terms of a single frequency measurement. Several of the theoretical problems considered by Bloch are illustrated experimentally in the work of Anderson (6, 7) and Arnold (8).

Anderson (7) has observed multiple quantum transitions in the proton resonances of 2-bromo-5-chlorothiophene and *p*-chlorobenzoyl chloride at high rf levels. In these substances chemical shifts and spin-spin couplings are of comparable magnitude. An  $n$ -fold quantum transition between energy levels  $(E_0)_k$  and  $(E_0)_l$  represents the absorption of  $n$  quanta of frequency  $\nu$



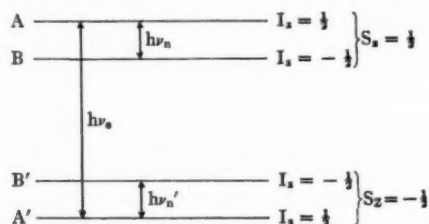
where  $\hbar((E_0)_k - (E_0)_l) = n\hbar\nu$ . A simple general discussion of multiple quantum perturbation theory is given by Dirac (9). It is possible that, in Bloch's notation, multiple quantum transitions will be found when  $\mathcal{H}_D(t)$  is so large that it cannot be included in  $\mathcal{H}E_1$  so as to satisfy conditions 6 and 7.

Wangsness (10, 11) has discussed the macroscopic equations of motion for MR, and the time rate of change of the spin density matrix  $\sigma$  from the point of view of irreversible thermodynamics. He has proposed that by invoking the principle of "minimum entropy production" one can test the adequacy of equations purporting to describe the dynamics of relaxation, and can improve on the generality of the Wangsness-Bloch (4) equation for  $\sigma$ . Irreversible thermodynamics has been used by Barker & Mencher (12) to discuss the Overhauser effect, including the case where the nucleus-electron interaction is due to dipolar coupling.

Torrey (13) has modified the phenomenological Bloch equations to include the effects of self-diffusion and spin exchange. Effects of this sort are important in attenuating echo amplitudes when spin-echo experiments are carried out in nonuniform magnetic fields. Portis (14) has considered the effects of diffusion of spin excitation through dipolar coupling on the Bloch equations in connection with the electron spin resonance line shapes of F-centers.

Herzog & Hahn (15) have made a theoretical and experimental study of double nuclear resonance in solids which contain two types of magnetic spins, A and B. They consider in particular the case for which the static broadening of A is exclusively due to dipolar interaction with the B spins. The spin echo formed at a given time from the A spin ( $\text{Cl}^{35}$  in  $\text{NaClO}_3$ ) while the B spins ( $\text{Na}^{23}$ ) are subjected to cw excitation depends strongly on the intensity of this excitation. Hahn & Kaplan (16) show that when the nutational frequency  $\gamma_B H_1$  of the B spin system is equal to the precessional frequency  $\omega_A$  of the A spin system, the  $I_z^B I_{\pm}^A$  part of the AB dipole-dipole interaction becomes secular and one obtains a maximum in the effective  $T_1^{-1}$  relaxation of the A system spins.

Feher (17) has developed an extremely interesting technique whereby a nuclear resonance can be observed through its effect on an EMR line intensity. Consider the four Zeeman and hyperfine energy levels indicated below corresponding to an electron and nucleus with spins  $S = \frac{1}{2}$ ,  $I = \frac{1}{2}$ .



Partially saturate the microwave resonance transition with frequency  $h\nu$ , corresponding to  $A \leftrightarrow A'$ . The observed microwave resonance intensity will be determined by the relative steady state populations of A and A', and these relative intensities will normally be determined by the microwave intensity and natural relaxation processes. If, however, one determines the steady-state microwave absorption intensity corresponding to  $A \leftrightarrow A'$ , and simultaneously carries out a rapid passage adiabatic nuclear resonance with rf corresponding to  $\nu_n$ , the populations of the A and B levels will be inverted and there will be observed a corresponding modification of the microwave absorption intensity. By using this technique, Feher has indirectly observed the  $P^{31}$  resonance in phosphorus-doped silicon, has measured the otherwise nonobserved hyperfine coupling in lithium-doped silicon, and has also observed  $Si^{29}$  hfs. This double resonance method apparently also resolves potassium and chlorine hfs from F-center electrons. Feher (18) has also devised a new technique for polarizing nuclei in paramagnetic substances. This method requires that one be able to sweep through a finite range of magnetic field in a period short compared to either the electron or nuclear relaxation times. One starts on the high field side with the four spin states  $A'$ ,  $B'$ , B, A having essentially the relative populations  $(1+\epsilon)$ ,  $(1+\epsilon)$ ,  $(1-\epsilon)$ ,  $(1-\epsilon)$ , where  $\epsilon$  is determined by the Boltzmann distribution factor with the electronic magnetic moment. Rapid adiabatic passage with decreasing field through the microwave spin resonance transition  $A \leftrightarrow A'$  inverts the populations of these two states, leading to the new sequence of populations  $(1-\epsilon)$ ,  $(1+\epsilon)$ ,  $(1-\epsilon)$ ,  $(1+\epsilon)$ . Finally, rapid adiabatic passage through the rf transition  $B \leftrightarrow A$  inverts these two populations, and one obtains the sequence of populations  $(1-\epsilon)$ ,  $(1+\epsilon)$ ,  $(1+\epsilon)$ ,  $(1-\epsilon)$ . Now the nuclear spin states with  $I_z = +\frac{1}{2}$ , i.e., A and A', have populations  $(1-\epsilon)$ , and the nuclear spin states with  $I_z = -\frac{1}{2}$ , B and B', have populations  $(1+\epsilon)$ . This technique has been used by Feher & Gere (19) to polarize  $P^{31}$  nuclei in phosphorus-doped silicon. The nuclear polarization can be measured by relative hfs multiplet intensities in the EMR.

Wertz, Jain & Batdorf (20) have observed an interesting transient effect in the NMR spectrum of methyl alcohol under certain sweep conditions with large rf intensity. The amplitude of the hydroxyl proton resonance is markedly dependent on the direction of sweep. These authors suggest that spin-spin coupling between methyl and hydroxyl protons leads to a modification of the hydroxyl proton spin states when the methyl proton resonance is traversed.

*Chemical structure and spin relaxation.*—Several types of spin tensor couplings can contribute to  $\mathcal{H}_G$  in equation 2 in addition to simple magnetic dipole and electric quadrupole interactions. Such interactions can be important for both electron and nuclear spin relaxation. For example, paramagnetic relaxation in metal ions in liquid solutions can be brought about by a variety of time-dependent anisotropic interactions associated with bulk tumbling of metal ion complexes, and with the formation and dissociation

of these complexes. In principle, this relaxation can be calculated from the time-dependent terms in an effective spin Hamiltonian. McConnell (21) has suggested the importance of anisotropic hyperfine interactions (as well as anisotropic  $g$ -factors) in giving  $T_1$  and  $T_2$  broadening in the EMR of cupric hydrates and complexes in solution. Strikingly different hyperfine line widths have been observed by McGarvey (22) in the EMR spectra of cupric chelates in solutions.

Similarly, anisotropic chemical shifts can contribute to  $\mathcal{H}_G$ , and hence, to nuclear relaxation. McConnell & Holm (23) have found evidence for this mechanism of nuclear relaxation in substances containing  $C^{13}$ :  $C^{13}$  in its natural abundance in oxygen-free  $CS_2$  shows a relatively short  $T_1$  ( $\sim 60$  sec.), even though the concentration of magnetic nuclei is extremely small. Also,  $C^{13}$  nuclei in symmetrical environments with isotropic chemical shifts [ $CCl_4$ ,  $C(CH_3)_4$ ] show unusually long relaxation times. Gutowsky & Woessner (24) have also discussed this mechanism for  $F^{19}$  nuclear relaxation in 1,3,5-trifluorobenzene and in Freons (fluorochloromethanes). In a substance such as  $CHFC l_2$ , one would expect  $T_1$  for  $H^1$  and  $F^{19}$  to be essentially the same, since the spin magnetic moments of the two nuclei are nearly equal. Instead, the  $F^{19}$  relaxation times are almost ten times shorter than the  $H^1$  relaxation times. Gutowsky & Woessner also find that  $T_1^{-1}$  for  $F^{19}$  increases with increasing resonance frequency  $\omega_0$ ; this is what one expects for anisotropic chemical shift relaxation since a straightforward application of the Bloembergen, Purcell & Pound (3) type calculation to this problem gives for  $T_1$  (23, 24):

$$T_1^{-1} = 2/15(\Delta\sigma)^2\omega_0^2\tau_c(1 + \omega_0^2\tau_c^2)^{-1} \quad 8.$$

Here  $\tau_c$  is the molecular correlation time and  $\Delta\sigma$  is the anisotropy in the nuclear shielding (assumed axially symmetric). Gutowsky & Woessner show that the shift anisotropies inferred from the observed relaxations, and equation 8, i.e.,  $\Delta\sigma \sim 7 \times 10^{-4}$ , are of the same order as those expected from the work of Saika & Slichter (25) on  $F^{19}$  shielding due to the second-order paramagnetic effect of covalent fluorine  $p$ -electrons. It is possible that effects other than those considered above may contribute to the marked differences in  $H^1$  and  $F^{19}$  relaxation times in the Freons. If significant contributions to these relaxations come from intermolecular dipole interactions, then the mechanical (inertial) anisotropies of the molecules could lead to different  $H^1-H^1$ ,  $H^1-F^{19}$ ,  $F^{19}-F^{19}$  intermolecular correlation times. This can be seen by considering a simplified example: in a hypothetical molecular liquid of diatomic  $H-F$  molecules, the linear spacial velocities of the  $H^1$  nuclei are  $\sim 19$  times faster than are those of  $F^{19}$  nuclei, due to molecular rotation. Such differences in linear velocities could lead to shorter intermolecular correlation times, and longer relaxation times, for protons. It is not at all certain whether this effect could actually be important in liquid  $HF$  (discussed later in the section on the Overhauser effect), or in the liquid Freons where the molecular mechanics is a little involved. Other sorts of molecular-

and liquid-structure properties that are related to relaxation effects are illustrated below.

Nolle & Morgan (26) have determined  $T_1$  and  $T_2$  for protons in aqueous solutions of  $\text{Cr}^{+++}$ ,  $\text{Mn}^{++}$ , and  $\text{Co}^{++}$  in the *ca.* 5 to 30 Mc. range.  $T_2$  was constant in each case throughout this range whereas in going from 30 Mc. to 5 Mc.  $T_1/T_2$  decreased from 3.7 to 1.5 in  $\text{Cr}^{+++}$  solutions, and from 10 to 2 in  $\text{Mn}^{++}$  solutions. Little change was noted for the  $\text{Co}^{++}$  solutions. Bloom (27) has extended this work down to the earth's field region (2200 c.p.s.) for aqueous  $\text{Mn}^{++}$  solutions and finds  $T_1 = T_2$  at the lowest field.  $T_2$  is approximately constant over the entire field range, and  $T_2 N = 1.5 \times 10^{-5}$  sec. where  $N$  is the formal  $\text{Mn}^{++}$  concentration. This equation holds for  $N = 0.5 - 1.0 \times 10^{-4}$  formal, for pH = 1 to 7, and for a variety of anions. In this work, Nolle, Morgan & Bloom suggest that these relaxation effects can be interpreted in terms of a correlation time  $\tau$  during which a proton in a water molecule is closely associated with the paramagnetic ion as water of hydration. Bloom (27) reports  $\tau = 2.1 \mu\text{sec.}$  for the  $\text{Mn}^{++}$  hydrate.

Morgan *et al.* (28) have determined proton relaxation times in aqueous solutions of Cr(III) complexes and assert that the efficiency of proton relaxation increases in the order expected for increasing interaction between solvent protons and complex:  $\text{Cr}(\text{CN})_6^{3-}$ ,  $\text{Cr}(\text{en})_3^{3+}$ ,  $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ ,  $\text{Cr}(\text{NH}_3)_6^{3+}$ ,  $\text{CrF}_6^{3-}$  and  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ .

Morgan, Murphy & Nolle (29) have determined proton relaxation times in water-glycerine solutions containing either  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ , or  $\text{Cr}(\text{en})_3^{3+}$  as paramagnetic relaxing agent. The solutions containing  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  showed two distinct  $T_1$  relaxation times, one due to protons bonded to carbon atoms which do not exchange with the hydration sphere of  $\text{Cr}^{3+}$ , and another shorter  $T_1$  due to protons which do exchange. On the other hand, solutions containing  $\text{Co}(\text{en})_3^{3+}$  showed only one  $T_1$  since in this case no solvent protons can exchange with the complexing agent. Similar results are observed for  $T_2$ . The shortest  $T_1$  in the  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  water-glycerine system shows a rather complex dependence on solution viscosity.

Broersma (30) has made a theoretical and experimental study of nuclear magnetic relaxation in heterogeneous systems. It is pointed out that in general the average relaxation time observed is dependent on the method of measurement: (a) Local relaxation effects can be completely averaged out within the time of measurement, and the system behaves macroscopically as though it had a single relaxation time which is the time average of the local relaxation times. (b) In measurements which are fast relative to the rate of averaging local relaxation effects (i.e., a fast passage resonance), the system can behave as a collection of isolated systems, each with its own relaxation time and time-dependent magnetization. In intermediate cases the relaxation processes are best characterized by the concept of the "amount of relaxation during time  $t$ ." Broersma shows that protons in hydrocarbons mixed with paramagnetic crystals, and dilute solutions of paramagnetic ions in water, behave as two (relaxation time) phase systems.

Wertz (31) has studied the relative effect of numerous paramagnetic ions in producing  $\text{Cl}^{35}$  nuclear relaxation in aqueous sodium chloride solutions. Complex formation, including hydration, appears to play an important role in determining the relative effectiveness of different paramagnetic ions.

Giulotto, Lanzi & Tosca (32) have measured proton relaxation times for chlorobenzene and phenol at various concentrations in carbon tetrachloride. (Different kinds of protons were not distinguished.) The  $T_1$  for both systems is discussed in terms of the relative contributions of molecular rotation- and translation-stimulated relaxation, and the  $T_1$ -viscosity-concentration behavior is considered to show the absence of polymerization in chlorobenzene, and the occurrence of polymerization in phenol.

Nederbragt & Reilly (33) have determined aromatic and methyl group proton  $T_1$  relaxation times in the pure liquids benzene, toluene, *p*-xylene, mesitylene, and in solutions of benzene and *p*-xylene dissolved in  $\text{CS}_2$ . In all cases,  $T_1$  for the aromatic protons exceeds  $T_1$  for the methyl group protons; dilution in  $\text{CS}_2$  brings about a profound increase in the relaxation times. In unpublished work, Reilly has related the "infinite dilution" relaxation times to average proton-proton internuclear distances, assuming intramolecular dipole-dipole relaxation (private communication).

Nuclear  $T_1$  and  $T_2$  relaxation in liquids which is directly or indirectly dominated by quadrupole interactions is especially interesting from a chemical point of view since quadrupole couplings have at least a close qualitative connection with molecular electronic structure. Also, the analysis of such relaxation in terms of molecular motion and environment in the liquid state tends to be rather simple since one does not have to be concerned with long range field effects.

Roberts (34) has observed proton resonances for N—H protons in a variety of compounds at different temperatures. In general, such resonance lines are modified by (a) N—H spin-spin coupling, (b)  $\text{N}^{14}$  quadrupole relaxation, and (c) the rates of N—H proton chemical exchange. Roberts shows that broad N—H proton lines in pure liquid amides and in pyrrole are due to  $\text{N}^{14}$  quadrupole relaxation effects, rather than proton chemical exchange of intermediate frequency.

Wertz & Jardtzy (35) have investigated the relation between solution composition and  $\text{Na}^{23}$  resonance line widths found in aqueous solutions of sodium ion. Different anions differ greatly in their broadening effect on the  $\text{Na}^{23}$  resonances, and it is felt that the relaxation originates in nuclear quadrupole interactions in the electrically distorted  $\text{Na}^+$  ion in the complex, or ion pair, which is formed in solution.

The work of Itoh & Yamagata (36) also nicely illustrates possible relations between chemical structure and quadrupole-induced nuclear relaxation. These authors have observed bromine NMR in three phases of ammonium bromide: I (NaCl type, above  $138^\circ\text{C}$ .); II (CsCl type,  $-38^\circ\text{C}$ . to  $138^\circ\text{C}$ .); III (tetragonal, below  $-38^\circ\text{C}$ .). In going from I to II the "paramagnetic" chemical shift increases from  $1.3 \times 10^{-4}$  to  $2.3 \times 10^{-4}$ , and the  $\text{Br}^{81}$  nuclear

relaxation time decreases by a factor of about one hundred (shift measured relative to aqueous  $\text{Br}^-$ ). In II, the  $\text{Br}^{81}$  relaxation is ascribed to a time dependence of the quadrupole coupling which originates in  $\text{NH}_4^+ - \text{Br}^-$  covalent bonding, and the motions of the ammonium ions. In this phase the  $\text{Br}^{81}\text{T}_1$  shows an exponential dependence on temperature which is the same as that found from proton NMR to correspond to reorientations of ammonium ions. In phase III, where the quadrupole interaction is large, a resonance shift of the transition,  $m = \frac{1}{2} \leftrightarrow -\frac{1}{2}$ , was studied as a function of temperature and interpreted to give the temperature dependence of  $\text{eqQ}$ .

Masuda (37) has determined  $\text{T}_1$  and  $\text{T}_2$  for chlorine in  $\text{TiCl}_4$ ,  $\text{VOCl}_3$ ,  $\text{CrO}_2\text{Cl}_2$ , and  $\text{SiCl}_4$ .  $\text{T}_1 = \text{T}_2$  and line widths are nearly proportional to the square of the quadrupole couplings.

Spin relaxation in paramagnetic solids can sometimes also be related to electronic structure. Shulman & Wyluda (38) have determined  $\text{T}_1$  for  $\text{Si}^{29}$  in *n*- and *p*-type silicon as a function of carrier concentration.  $\text{Si}^{29}$  relaxation by the carriers is presumed to arise through I·S hyperfine interactions, and the observed weaker relaxation in *p*-type silicon is considered to be due to the *p* nature of the hole wave functions. For some reason neutral indium acceptors do not act as perfect paramagnetic sinks to relax  $\text{Si}^{29}$  nuclei by spin diffusion. Honig & Combrisson (39) have reported unusually long electronic  $\text{T}_1$  relaxation times in As-doped silicon.

Redfield (40) has determined  $\text{T}_1$  for  $\text{Al}^{27}$  and  $\text{Cu}^{63}$  in aluminum and copper metal at  $2^\circ$  and  $4.2^\circ\text{K}$ . using the adiabatic fast-passage technique.  $\text{T}_1$  is inversely proportional to the absolute temperature, from  $2^\circ$  to  $300^\circ$ , in accordance with the Korringa theory.

Proton resonance is frequently used for studies of crystal structure and internal motions in solids. Elleman & Williams (41) have analyzed the proton NMR of brucite  $[\text{Mg}(\text{OH})_2]$  to obtain information on proton lattice positions in this substance. It is concluded that the protons are arranged in parallel planes with hexagonal symmetry, and the smallest interproton distance within planes is  $3.12 \pm 0.01$  Å, and between planes is  $1.93 \pm 0.02$  Å. A study of proton relaxation in water adsorbed on  $\text{TiO}_2$  is reported by Mays & Brady (42). At low coverages and at  $77^\circ\text{K}$ ., it is concluded from proton relaxation that the effective correlation time is rather short (relatively free  $\text{H}_2\text{O}$ ) whereas at higher coverages the correlation time is increased because of "ice" formation. Fuschillo & Aston (43) have also studied proton line widths for materials adsorbed on  $\text{TiO}_2$ . Oshima & Kusumoto (44) have observed effects of elongation on the temperature dependent proton line widths in natural rubber. Aston, Segall & Fuschillo (45) have studied proton NMR of crystalline solid solutions of 2,2-dimethylbutane in 2,3-dimethylbutane in the  $10^\circ\text{K}$ . to  $273^\circ\text{K}$ . temperature range.

*Overhauser effect.*—Solomon & Bloembergen (46) have determined  $\text{H}^1$  and  $\text{F}^{19}$  relaxation times in anhydrous and aqueous HF solutions, and have observed the nuclear steady and transient Overhauser effect. In pure anhydrous HF isotropic spin-spin (exchange) coupling dominates the relaxation

whereas in the presence of small concentrations of water the relaxation is dipolar. The experimental results can be interpreted to yield a value for the (molecular, or polymeric) H—F spin-spin coupling constant (615 c.p.s.) and an activation energy for proton transfer. HF solutions containing some water show  $H^1$  relaxation times much longer than those of  $F^{19}$ , a fact attributable to the more rapid spatial motions of the protons.

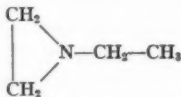
Carver & Slichter (47) have observed the electron-nuclear Overhauser effect (leading to enhanced nuclear polarization) for the following systems: metallic Li and Na, and Na dissolved in liquid ammonia. NMR of  $Li^7$ ,  $Na^{23}$ , and  $H^1$  were observed in the three cases. Partial  $Li^7$  and  $Na^{23}$  polarizations were obtained in the metals, and in concentrated solutions of sodium in ammonia, a nearly complete  $H^1$  polarization was observed.

*Rates of fast chemical processes by MR.*—In certain cases MR effects can be used to make direct and accurate determinations of the rates of fast chemical processes which take place under steady state conditions. This section is devoted to a discussion of such processes; they include the chemical exchange of nuclei between different molecular species, electron transfer and exchange, and molecular internal rotation and inversion, as well as group reorientations in solids (included in the previous section).

A well-known technique for measuring chemical exchange of nuclei involves a study of the effect of this exchange on spin-spin multiplet structure in NMR. Arnold (8) has published quantitative experimental data which lead to an evaluation of the rates of hydrogen ion and hydroxyl ion catalyzed hydroxyl proton exchange in ethyl alcohol. He has given a general formula—subject to the validity of the Bloch equations—for resonance line shapes under conditions where the resonant nuclear species can exchange between any number of possible magnetic environments.

Grunwald, Lowenstein & Meiboom (48) have made a careful and detailed study of the rate of proton exchange between methylammonium ion and water as a function of pH by examination of the effect of exchange on methyl group spin-spin multiplets.

Rate processes may also be determined through their effect on multiplets due to chemical shifts. Bottini & Roberts (49) have been able to determine the rate of ammonia-like inversion in N-ethylethylenimine:



The protons *cis* and *trans* to the N-ethyl group show resolved chemical shifts at room temperature, which collapse at higher temperatures. The inversion frequency is estimated to be  $\sim 25$  c.p.s. at  $110^\circ\text{C}$ . A much higher inversion frequency is reported for N-ethylalleneimine.

Gutowsky & Holm (50) have studied internal rotation about the C—N bond in N,N-dimethylformamide (DMF) and in N,N-dimethylacetamide



(DMA) by determining the effect of temperature on the apparent splitting of the chemically shifted N-methyl groups. Activation energies of  $7 \pm 3$  and  $12 \pm 2$  kcal. mole<sup>-1</sup> are reported for internal rotation about the C—N bond in DMF and DMA. The corresponding free energies of activation were found to be 22 and 19 kcal. Proton NMR of N-methylformamide, N-methylacetamide, N-methylformanilide and N-methylacetanilide indicates that these substances exist predominantly in one configuration.

Just as rate processes can be determined by their effect on nuclear spin-spin multiplets, so they can also be obtained by their effect on (nuclear-spin)-(electron-spin) hyperfine multiplets in EMR. Electron exchange or transfer frequencies of the order of hyperfine splittings (e.g., 1 to 100 Mc.) can sometimes be determined. Weissman & Garner (51) have attempted to use this method to estimate the rate of electron exchange between ions of  $W(CN)_6^{3-}$  in solutions of different concentrations.

A new method for the determination of the rates of "paramagnetic pulse" reactions has been developed by McConnell & Weaver (52) and by Bruce, Norberg & Weissman (53). In this method, one observes the resonance of a nuclear species which is part of the time in a diamagnetic molecule, D, and part of the time in a paramagnetic molecule, P. McConnell & Berger (54) have shown that under quite general conditions involving the hyperfine interaction in P, the observed  $T_2$  of the DP mixture will be exactly equal to the life time of D, with respect to  $D \rightarrow P$ . This leads to an evaluation of the forward (and reverse) rate constants for  $D \rightleftharpoons P$ . Using this technique, McConnell & Weaver measured the rate of electron transfer between Cu(I) and Cu(II) in concentrated hydrochloric acid solutions, and Bruce, Norberg & Weissman determined the rates of electron transfer between neutral and positive ion molecules of N,N'-tetramethylparaphenylenediamine. Holm *et al.* (55) have also used this approach in a preliminary study of the EMR and NMR of the equilibrium mixture  $N_2O_4 \rightleftharpoons 2NO_2$ .

*EMR of radicals.*—Luck & Gordy (56) have observed the EMR of radicals produced by x-ray irradiation of alcohols, amines, amides and mercaptans in the solid state. Hyperfine structure due to protons is observed and is ascribed, in various cases, to the ion radicals  $C_2H_4^+$ , and  $CH_2^+$ . It is not certain whether the latter radical is really "free," or attached to some other molecule. The EMR quintet for  $C_2H_4^+$  corresponds to a proton hyperfine splitting of about 25 gauss, and this is quite reasonable in terms of what is found for hfs in  $\pi$ -electron radicals (cf. next section). Drahmman, Anderson & Alger (57) have reported similar findings in various organic substances which were irradiated with 2-Mev. electrons. Gordy & McCormick (58) have observed  $C_2H_4^+$ -like hfs in irradiated  $Hg(CH_3)_2$ ,  $C_2H_5$ -like hfs from  $Hg(C_2H_5)_2$ , and  $CH_3$ -like hfs from  $Zn(CH_3)_2$ . Evidence for still other radicals is obtained from the EMR of irradiated  $Zn(CH_3)_2$  and  $Sn(CH_3)_4$ . Livingston, Ghormley & Zeldes (59) have used EMR to obtain evidence for the formation of  $HO_2$  radicals when the products of subjecting water and related substances to an electrical discharge are condensed at liquid nitrogen tempera-

tures. An unsymmetrical EMR resonance is observed, corresponding to a not-unexpected anisotropic  $g$ -factor for  $\text{HO}_2$ . Probably many peroxy radicals will show similar broad resonance resulting from anisotropic  $g$ -factors, and this line broadening may well be a useful diagnostic test for peroxy radicals in chemical systems. Pastor *et al.* (60) have studied the narrow EMR found in charred dextrose as a function of charring temperature and amount of adsorbed  $\text{O}_2$ ,  $\text{NO}$ ,  $\text{N}_2$ , and  $\text{H}_2$ . Adsorption of the two paramagnetic gases results in a marked increase in the EMR line width. Walter *et al.* (61) have discussed the relation between molecular structure and EMR line width in the solid state for a number of radicals derived from triphenylpicrylhydrazil, and the triphenylaminium ion.

Delbecq, Smaller & Yuster (62) have observed the hfs in the EMR of hydrogen and deuterium atoms produced by irradiation of U-centers (hydride ions) in KCl crystals at  $80^\circ\text{K}$ . Jen *et al.* (63) have reported the observation of hfs due to hydrogen and deuterium atoms condensed in their molecular matrices at liquid helium temperatures. Each hyperfine line is accompanied by two symmetrically spaced satellite lines. Additional sharp lines were observed around  $g=2$  which may arise from other molecular radical species derived from molecular hydrogen.

*Unpaired electron distributions in radicals.*—Important information regarding unpaired electron distributions in molecules, crystals, solutions and metals can be obtained from MR studies of electron-nucleus hyperfine interactions, which are usually observed as multiplet splittings in EMR and as resonance shifts in NMR. An especially interesting area in this regard is that of the aromatic proton splittings in the EMR spectra of aromatic free radicals in solution. Recent observations of such splittings include those in naphthosemiquinone ions by Wertz & Vivo (64), in aromatic negative ions by Tuttle, Ward & Weissman (65), and by de Boer (66), in diphenylnitric oxide by Hoskins (67), and in biradicals by Jarrett, Sloan & Vaughan (68). Because these hfs must arise from contact interaction, the unpaired  $\pi$ -electron in these radicals must have some  $s$ -character at the aromatic protons. Theoretical discussions of the origin of such aromatic proton hfs in terms of configuration interaction, or indirect exchange coupling have been given by Bersohn (69), McConnell (70), and Weissman (71). Venkataraman & Fraenkel (72) demonstrated experimentally by deuterium substitution in the  $p$ -benzosemiquinone ion that the observed aromatic proton hfs are not brought about by loss of  $\pi$ -electron orbital symmetry through out-of-plane hydrogen vibrations. McConnell (70, 73) has emphasized the important possibility that aromatic proton hfs may be used to measure electron densities at carbon atoms in aromatic (and olefinic) molecules, by an approximate equation of the form,

$$a_j = Q\rho_j, \quad 9.$$

where  $a_j$  is the hyperfine splitting (in gauss) of the electron resonance by the aromatic proton directly attached to the carbon atom  $j$ , and  $\rho_j$  is the unpaired

electron density in a  $p$ - $\pi$  orbital on carbon atom  $j$  ( $0 \leq \rho_j \leq 1$ ). Ideally,  $Q$  should be a "universal constant" whose value is the same for all CH bonds in all aromatic molecules. It would be foolhardy to suppose that this ideal situation is exactly true; it is quite reasonable, on the other hand, that large variations of  $a_j$  are due to variations of  $\rho_j$ , rather than the effective  $Q$ . This means that equation 9 is probably quite good for semiquantitative, or at least order-of-magnitude estimations of electron densities in aromatic molecules. The best empirical value for  $Q$  seems to be somewhere in the range  $Q = 30 \pm 5$  gauss; this value is in accord with earlier theoretical estimates (69, 70) and is also in accord with the recent and considerably more accurate (than 70) calculations of Jarrett (74) who obtains  $Q = 28$  gauss. Hyperfine splittings in benzosemiquinones are in accord with equation 9 and electron distributions calculated from simple Hückel MO theory (73). de Boer (66) has shown that simple Hückel theory and a linear relation as in equation 9 are in accord with the observed hfs in the negative ions of biphenyl, naphthalene, and anthracene (65, 66). As yet unpublished work by Weissman, de Boer & Conradi on the hfs in positive ions of anthracene, tetracene and perylene also supports the idea that  $a_j$  is closely related to  $\rho_j$  and suggests that  $Q$  for positive ions may be slightly larger than for negative ions. [The data of Luck & Gordy (56) for  $C_2H_4^+$  correspond to  $Q = 50$  gauss if this is a planar ion]. Yokozawa & Miyashita (75) have also observed EMR in sulfuric acid solutions of perylene, but did not report the hfs observed by Weissman, de Boer & Conradi. Additional unpublished work by Weissman and coworkers on benzene negative ion, and large aromatic negative ions, suggests that  $Q$  may depend somewhat on ring size.

It is also possible that electron distributions may be determined through observations of  $C^{13}$  hfs in aromatics; Tuttle & Weissman (76) have made the first step in this direction by determining the hfs due to  $C^{13}$  in the  $\alpha$ -position in naphthalene negative ion. This  $C^{13}$  splitting is 7.1 gauss.

Bennett, Ingram & Schonland (77) have observed EMR in alkali metal superoxides, and in chlorine dioxide in the solid state and in solutions. In the latter, chlorine hfs is resolved and these splittings, as well as the  $g$ -factor anisotropies, are interpreted in terms of molecular orbital theory.

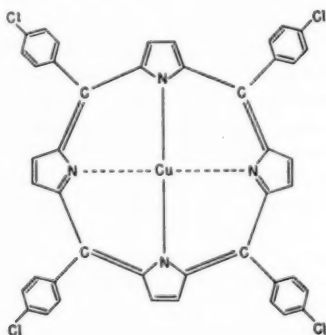
*EMR of metal ions, especially in crystals.*—There are so many experimental, theoretical, and review articles written on this subject from year to year that there is hardly space or need for this subject to be reviewed here. We therefore mention only a few articles which appear to be especially interesting from a chemical point of view.

George, Bennett & Ingram (78) have observed the EMR of three single crystal types of acidic ferrimyoglobin as a function of crystal orientation. The same  $g$ -value variation relative to the haem planes was found for each crystal although the haem orientations relative to the crystal axes were different for the different crystal types. The  $g$ -values are  $g_{\perp} = 2.00$  and  $g_{\parallel} = 6.00$ . The  $S = 5/2$  state of  $Fe^{+++}$  is strongly split by the haem "crystal field" and

the most intense of the observed transitions is thought to be between levels of the lowest doublet  $S = \pm \frac{1}{2}$  states.

Griffith (79) has given a theoretical discussion of the magnetic properties of haemoglobin compounds. He suggests that the oxygen molecule in oxyhaemoglobin is not at right angles to the haem but is probably parallel to it; all ferrihaemoglobin derivatives have a spin of either  $S = \frac{1}{2}$  or  $S = 5/2$  at each iron atom or, in the case of ferrihaemoglobin hydroxide, are a thermal equilibrium of the two; ferrihaemoglobin derivatives with  $S = 5/2$  have usually or always a large zero-field splitting, the lowest states being characterized by  $S = \pm \frac{1}{2}$  perpendicular to the haem.

Ingram *et al.* (80) have observed hfs in the EMR of copper *p*-chloro- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphin at 20°K.



The hfs is interpreted as arising from unpaired electron interaction with Cu and Cl nuclei. It is argued that the Cl hfs is not due to intermolecular Cu—Cl interactions. These conclusions, if correct, show that the molecular orbital containing the unpaired electron in this substance has appreciable amplitude at both the copper and chlorine atoms.

Weissman & Garner (51) have observed (isotropic) hfs due to  $W^{183}$  in solutions of  $W(CN)_6^{3-}$ . This result conclusively demonstrates that the odd electron in this complex ion has *s*-character.

Tinkham's EMR work on  $Mn^{++}$ ,  $Fe^{++}$ ,  $Co^{++}$ , and  $Cr^{+3}$  dissolved in  $ZnF_2$ , which leads to information on unpaired electron densities at the  $F^{19}$  nuclei through  $F^{19}$  hfs, has been published (81), but was reviewed by Hutchison last year (82). This sort of information on "long range" hfs, or "super hfs," can sometimes also be obtained from NMR. Thus, Shulman & Jaccarino (83) have observed  $F^{19}$  NMR in oriented single crystals of  $MnF_2$  in the antiferromagnetic state. A strong "paramagnetic shift" is found and is due to the partially unbalanced but oriented spin left on the F atom when there is charge transfer from  $F^-$  to  $Mn^{++}$ ; Bleaney (84) has pointed out that these results are in quantitative accord with the superhyperfine splittings

observed by Tinkham (81) in the EMR of  $Mn^{++}$  dissolved in  $ZnF_2$ . In further unpublished work on this subject Shulman has shown that the NMR results on  $F^{19}$  in  $MnF_2$  permit the determination of more elements of the hyperfine tensor coupling  $I \cdot A^N \cdot S$  than was possible in Tinkham's work, and one can then obtain rather detailed information on the *p*- and *s*-character of the unpaired spin distribution about  $F^{19}$  in  $MnF_2$ .

*Knight shifts, and metals.*—Information on unpaired conduction electron distributions is also obtained from NMR shifts when these shifts are dominated by hyperfine interactions.

Knight shifts of  $Ba^{135}$ ,  $Ba^{137}$ ,  $Cd^{111}$ , and  $Cd^{113}$  are reported by Rowland (85). The shifts are of the order of 0.4 per cent, and in the case of Cd are markedly anisotropic. Rowland suggests that this anisotropy may be caused by a greater density of the conduction electrons in the direction of the hexagonal axis, or possibly spin-orbit coupling effects. Also, the NMR line widths suggest exchange coupling between the two isotopes of Cd.

McConnell & Holm (86) have measured Knight shifts of  $Na^{23}$  and  $N^{14}$  in sodium-ammonia solutions as a function of sodium concentration. The experimental shifts are interpreted in terms of the contact densities of  $Na^{23}$  and  $N^{14}$  nuclei at the positions of the unpaired electrons. It is concluded that the unpaired electrons can be associated with  $Na^+$  ions in highly expanded orbitals similar to those appropriate to  $P^+$  ions in P-doped silicon. No Knight shift of the proton MR in these solutions was detectable, but a remarkably large and concentration-independent contact interaction for  $N^{14}$  was inferred from the large shifts of this nuclear species. This large interaction may be connected with charge-transfer between ammonia molecules and sodium ions; otherwise it must arise from some unknown specific interaction between ammonia molecules and trapped electrons.

Kjeldaa & Kohn (87) have calculated electronic wave functions at the Fermi surface for Na metal and have evaluated  $|\psi(0)|^2$  at the  $Na^{23}$  nucleus. The result is close to the value of this quantity which can be inferred from Knight shift measurements on sodium and the spin paramagnetic susceptibilities observed by Shumacher & Slichter (88).

Levy (89) has studied the 300 Mc. EMR of (a) pure Li and Na to temperatures above their melting points, (b) Li, Na, K, Rb, Cs and Ca in liquid ammonia, and (c) Li dissolved in methylamine. A very close parallel between resistivity and line width up to and above the melting point of sodium was found, which supports the Elliott-Yafet spin relaxation mechanism in this substance. Line widths in the solution spectra appear to be in accord with the model of Kaplan and Kittel. NMR and EMR show that in frozen alkali-metal ammonia solutions, the metal is precipitated out as small particles.

Owen *et al.* (90) have studied the EMR and NMR of dilute alloys of Mn in Cu with the purpose of investigating exchange coupling of the 3d electrons of  $Mn^{++}$  (presumed to be in the  $^6S$  state) with the 4s conduction electrons. The experimentally observed absence of the otherwise predicted

electronic Knight shift in the EMR, and Cu nuclear Knight shift, leads to the conclusion that the apparent 3d-4s (conduction electron) exchange interaction is much smaller than that appropriate to the free ion. The situation is fairly complicated, however, since the alloys show a complex antiferromagnetism and it is not entirely certain from the susceptibility measurements that Mn dissolves in Cu as  $Mn^{++}$  (6S). Knight, Androes & Hammond (91) and Reif (92) have observed Knight shifts in colloidal Hg at temperatures and fields corresponding to the normal and superconducting states. The onset of superconductivity gives rise to a resonance shift which implies a reduction in the spin paramagnetic susceptibility, or the contact hyperfine interaction, or both. It remains to be seen if this result will shed new light on the electronic structure of the superconducting state.

*Nuclear shielding and spin-spin coupling.*—The relation between chemical shifts and molecular electronic structure continues to be the subject of considerable theoretical interest as well as a matter of great practical importance. Das & Bersohn (93) have used a variational calculation to estimate the absolute value of the proton shielding in molecular hydrogen. The value so obtained is close to the best value reported by Ramsey; in addition the second-order paramagnetic term, as calculated by these authors using various hydrogen molecule wave functions, is in remarkably good agreement with the value of this quantity as obtained by Ramsey from the spin-rotational magnetic coupling. Similar variational calculations have been made by McGarvey, who has also used this method for more complex molecules (94). The general problem of proton shieldings in complex molecules appears to be uniquely difficult. This is because electrons relatively far removed from an individual proton can contribute substantial shieldings to that proton relative to the small shieldings produced by the very few electrons in the immediate vicinity of the proton. An extreme example of this effect is found in proton shieldings in aromatic hydrocarbons. Bernstein & Schneider (95), Bernstein, Schneider & Pople (96), and Reid (97) have tabulated proton chemical shifts in a number of aromatic hydrocarbons. Pople (98), and Bernstein, Schneider & Pople (96) have calculated relative proton shieldings in polynuclear aromatic hydrocarbons, where the shieldings are assumed to be dipolar and to originate in the diamagnetic anisotropy of the aromatic rings; these anisotropies were in turn estimated through a simplification of Pauling's classic calculation. McConnell (99) has shown that these long range shieldings can be derived directly from Ramsey's general shielding theory. Long range shieldings of the sort considered here also give rise to intermolecular shielding effects for liquids containing molecules which are mechanically and magnetically anisotropic. Experimental evidence for such intermolecular shielding effects has been obtained by Bothner-By & Glick (100), and also by Reilly (101). Corrections for these intermolecular shielding fields are necessary if one is to relate chemical shifts to molecular electronic structure; such corrections must be made experimentally by extrapolation to infinite dilution in an "inert" solvent, which ideally contains spherical

molecules of zero magnetic susceptibility. Otherwise one needs a detailed theory of liquid structure and molecular magnetic anisotropy.

Corio & Dailey (102) have interpreted aromatic proton chemical shifts in a number of monosubstituted benzenes under the assumption that these proton shieldings are proportional to the electron densities at the protons. The quantitative results are certainly in qualitative accord with this assumption: electron withdrawing substituents give a reduction in the proton shielding, and electron donating groups give increased shieldings. This may be another case where chemical reasoning is far ahead of rigorous physical theory although the above references to long-range shielding effects make one wonder just what electron densities are measured by the observed shieldings. Some of the uncertainties regarding the origin of proton shieldings might, at least in principle, be resolved through a study of the anisotropy of these shieldings. Coric & Dailey (103) have studied the effects of solvent composition on chemical shift determinations for monosubstituted benzenes.

Proposals that steric repulsions between H or F atoms are in some way associated with shielding effects have not been accompanied by any detailed theoretical reasons for believing that such effects should be particularly important (97, 104).

Muller, Lauterbur & Goldenson (105) have interpreted  $P^{31}$  chemical shifts in a variety of phosphorus compounds using the (ionic-character)-(unbalanced  $p$ -orbital) model of Saika & Slichter. For  $PX_3$  compounds the shifts are related to the ionic character of the  $P-X$  bond, and to the  $X-P-X$  angle. Van Wazer *et al.* (106) have published an extensive compilation of  $P^{31}$  resonance shifts in a large variety of compounds. Phosphorus atoms directly bonded to three atoms show large variations in nuclear shieldings, and large shifts relative to orthophosphate were observed for phosphorus connected to more than four other atoms, or connected to other atoms through bent bonds.

Holzman *et al.* (107) have reported  $Si^{29}$  chemical shifts in a variety of substances. Schnell & Rochow (108) have reported  $F^{19}$  shifts for the complete series  $SiF_x(Me)_{4-x}$  and  $SiF_x(Et)_{4-x}$ . Dudley, Shoolery & Cady (109) have reported the  $F^{19}$  NMR of  $SO_2F_2$ ,  $SOF_4$  and  $SOF_6$ . Phillips (110) has assigned chemical shifts and spin-spin coupling constants in the  $F^{19}$  NMR spectra of a large number of tetrafluorocyclobutanes. Tiers (104) has reported  $F^{19}$  shifts in various perfluoroalkanes.

Ogg & Ray (111) have observed  $N^{14}$  MR in various systems in which the molecular species giving the resonances are believed to be  $NO_2^+$ ,  $HNO_3$ ,  $N_2O_5$  and  $NO_2^-$ . When  $N_2O_5$  is dissolved in  $HNO_3$ , a single sharp  $N^{14}$  MR is observed, and this implies rapid  $N^{14}$  exchange between the species  $NO_2^+$ ,  $HNO_3$ , and  $NO_2^-$ .

Proton MR shifts are used by Huggins, Pimentel & Shoolery (112) in a study of hydrogen bonding effects in *o*-, *m*-, and *p*-chlorophenol, *o*-cresol, and acetic acid. Bader *et al.* (113) have used proton MR to establish the 3-butenolactone structure for diketone in the liquid state. Bernstein &



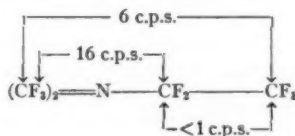
Schneider (114) have assigned proton chemical shifts to various aromatic ring positions in a series of methyl and deuterio pyridines. Cohen & Reid (115) have used proton shifts in water, alcohols and phenol to study hydrogen bondings in these substances as a function of concentration in inert solvents. Anderson (6) has analyzed the high resolution NMR spectra of a number of hydrocarbons to obtain chemical shifts and spin-spin coupling constants, and in several substances these quantities were of comparable magnitudes so that the observed spectra were relatively complex.

McConnell (116) has used molecular orbital theory to develop an approximate but quite general formulation of the relation between spin-spin coupling constants and molecular electronic structure. In the general case several distinct kinds of electron and nuclear interactions can contribute to the nuclear spin-spin couplings: one nucleus interacts magnetically with the spin or orbital motion or both, of an electron; this magnetically perturbed electron can interact magnetically directly with a second nucleus (giving coupling), or it can interact electrostatically with a second electron, which in turn interacts by spin or orbital magnetism with the second nucleus, giving coupling. Calculated couplings between nuclei show many peculiar properties; for example, two-electron spin coupling of nuclei due to electrons in *p*-orbitals depends on the angle  $\vartheta$  between the *p*-orbital axes as  $(1-3 \cos^2 \vartheta)$ . Thus, bond angles can play an important role in nuclear spin-spin couplings. Proton-proton couplings appear to be the easiest to understand from a theoretical point of view since they are probably all positive and simply related to a generalized "bond-order." Long range couplings between nuclear spins in molecules, i.e., spin-spin couplings that travel through several chemical bonds, are intimately connected with the chemical notion of electron delocalization, and usually require a long range correlation of electron spins. It is essentially for this reason that these couplings are so interesting from a theoretical point of view. Electron spin correlations for electrons on adjacent nuclei in a molecule are well known and are essentially the ingredients of the "electron pair bond"; nuclear couplings can give us direct evidence for such spin correlations over much larger distances in molecules.

A tabulation of H—H, H—F and F—F spin-spin couplings in a number of halogenated olefins has been given by McConnell, Reilly & McLean (117). Williams (118) has developed the MO theory of spin coupling with particular reference to H—H, H—F and F—F spin-spin couplings in aromatic hydrocarbons, and has also considered various aspects of the problem of the analysis of observed spectra in terms of spin-spin couplings and chemical shifts. Gutowsky & Williams (119) have considered the problem of the determination of the relative signs of nuclear spin-spin coupling constants, and have applied these considerations to the NMR spectrum of 1,4-difluoro-2,5,6-trichlorobenzene. In this substance

$$|J_{ortho}^{HF}| = 8.5 \text{ c.p.s. and } |J_{meta}^{HF}| = 6.2 \text{ c.p.s.};$$

it is shown that the signs of the two coupling constants are the same. Saika & Gutowsky (120) have found the following set of  $F^{19}$ — $F^{19}$  spin-spin couplings which further illustrate the complex nature of indirect nuclear coupling:



McConnell & Reilly (121) report an unusual and as yet unexplained  $F^{19}$  multiplet spectrum for  $CF_3CCl=CFCl$ . Ogg & Ray (122) have observed the  $F^{19}$  resonance of  $FNO_2$  and have proposed that the large  $F^{19}$ — $N^{14}$  spin-spin coupling (225 c.p.s.) shows that these two nuclei are directly bonded to one another.

Glick & Bothner-By (123) have measured  $CH_3 \leftrightarrow CH_2$  and  $CH_3 \leftrightarrow CH$  proton-proton splittings in 30 compounds and find all the couplings to be in the range 5.98 to 7.41 c.p.s. The small variations in these remarkably constant couplings can be empirically accounted for in terms of the Huggins electronegativity for the group attached to ethyl, or isopropyl.

*Absolute intensity measurements.*—Gardner & Fraenkel (124) have measured the EMR absorption intensity of liquid sulfur as a function of temperature in the range 189 to 414°C. These data were used to obtain the heat of scission of sulfur-sulfur bonds in polymeric chains (33 kcal./mole) and an absolute value of radical concentrations. The EMR line widths (40 to 100 gauss, 216 to 414°C.) are analyzed in terms of the rates of radical displacement reactions; the present reviewer does not agree with this analysis since there does not seem to be any evident way whereby a radical displacement reaction could serve as a strong "spin collision," and thus a line broadening process. Of course, radical recombination would serve as a strong collision since it is essentially a spin annihilation process.

Shumacher & Slichter (125) have determined the electron spin paramagnetic susceptibilities of lithium and sodium. Absolute intensity calibration was obtained by measuring the Li and Na nuclear resonances with the same samples and apparatus at the same frequency.

Livingston & Zeldes (126) have added more weight to the already well-known fact that diphenylpicrylhydrazyl is by no means a "simple" primary standard for EMR intensities. For single crystals of this substance they report sizable anisotropy in line width which parallels the  $g$ -factor anisotropy.

*Miscellaneous.*—The effect of radiation damping in limiting resolution in ultrahigh-resolution NMR has been discussed by Bruce, Norberg & Pake (127). It is indicated that with the resolution already available in some spectrometers, radiation damping may determine the width and maximum intensity of some otherwise strong resonances such as the proton resonance

of water. It is also pointed out that to reduce the radiation damping effect, it is necessary to decrease those spectrometer parameters which are normally maximized for best signal/noise, so that along with the saturation problem, adequate spectrometer sensitivity may be an eventual problem in ultrahigh-resolution work.

Reilly (128) has described a technique for determining small multiplet separations in high resolution NMR by measuring beats in the nuclear "ringing" signals observed in fast passage. For example, Reilly measured the  $\text{CF}_3 \leftrightarrow \text{CF}_2$  coupling in  $\text{CF}_3\text{—CF}_2\text{COOH}$  to be 1.48 c.p.s. using this technique under conditions where the individual multiplet lines could not be resolved to measure  $J$  directly.

Morin *et al.* (129) have described a sample cell especially suited for measurements of NMR chemical shifts.

Williams & Gutowsky (130) have investigated the production of sidebands by sample spinning in a nonuniform magnetic field.

Laukien (131) has made an experimental and theoretical study of the excitation of free precession of nuclear magnetization as a function of the length, intensity and frequency of the inducing impulses.

Anderson (6) has demonstrated the use of a new and simple procedure whereby the magnitude of a radio-frequency field  $H_1$  at a sample may be accurately determined with the aid of a small auxiliary radio-frequency field. Anderson & Arnold (132) have shown that a study of proton  $T_1$  in  $\text{H}_2\text{O—D}_2\text{O}$  mixtures supports the idea that proton relaxation in this system is due to dipole interaction.

Proctor & Robinson (133) have observed ultrasonic saturation of the nuclear magnetic spin levels of  $\text{Na}^{23}$  in a single crystal of  $\text{NaCl}$ . The  $\Delta m = 2$  transition is excited by ultrasonic lattice energy through nuclear electric quadrupole interactions. The observed transition rate appears to be explicable in terms of field gradients generated at the  $\text{Na}^{23}$  nuclei by displacement of point charges on the surrounding ions, and no large "covalent or anti-shielding" factor is required to explain the electrostatic interaction.

Ramsey (134) has developed the concept of negative absolute temperatures in thermodynamics and statistical mechanics, and particular attention is given to the application of this concept to the discussion of nonequilibrium states of magnetic spin systems in an applied magnetic field. From the thermodynamical point of view, negative absolute temperatures are realized whenever a system can have a maximum in entropy with a finite internal energy. Quantum statistical mechanics of the canonical ensemble will admit negative absolute temperatures providing the systems of the ensemble have a finite number of energy levels, each of finite energy, and providing there exist real systems of negative absolute temperature which can serve as large heat baths. In spite of certain possible philosophical objections regarding the applicability of the concept of negative absolute temperatures to real nuclear spin systems, it is certainly true that this concept has generally

won acceptance as the basis of a convenient temperature scale in magnetic resonance laboratories.

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# RADIATION CHEMISTRY<sup>1</sup>

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A number of review articles on radiation chemistry appeared during the past year. Hochanadel & Lind (1) and Miller (2) published summaries on radiation chemical research reported during 1955. Collinson & Swallow (3) surveyed the available literature on the radiation chemistry of organic systems. The action of ionizing radiation on biological materials was reviewed by Butler (4). Brooks (5) reviewed the recent literature on radiation effects in solids, and Burton & Neubert (6) published a résumé of the early investigations of the effect of fast neutrons on graphite. The Geneva Conference discussions on radiation effects in reactor materials, liquids, and solids were published (7); a large part of this material, particularly that on water and aqueous systems, was discussed in the preceding review of this series (1). Also of importance to the radiation chemist are the recent books: *Radiation Dosimetry*, edited by Hine & Brownell (8); *Rayonnement de Particules Atomiques Electrons et Photons* by Berthelot, (9); *Solid State Physics* edited by Seitz & Turnbull (10) which contains a chapter by Seitz and Koehler on radiation effects in solids. The closely related field of hot atom chemistry, recently covered in a comprehensive review by Willard (11), is not included as a separate subject in the present survey.

## GASES

Processes induced by absorption of ionizing radiation in gases have been subjected to extensive inquiry during the past year. The total relative ionization cross-sections of a wide variety of substances, including hydrocarbons and their substitution derivatives, were determined by Otvos & Stevenson (12) for single electron impact by slow electrons (50 to 100 v.) and for total ion production by  $\beta$ -particles emitted by  $C^{14}$  and  $Sr^{90}$ — $Y^{90}$ . It was found (a) that the observed ionization cross-sections for atomic gases can be calculated to a good approximation by taking the weighted sum of the outer or valence electrons of the atoms where the weights are the mean square radii of the electrons, and (b) that the relative total ionization cross-sections of molecules are constitutive molecular properties, i.e., the sum of the atomic cross-sections. The additivity of relative ionization cross-sections of the hydrocarbons applies without correction for unsaturation or other structural effects including those of isomerism. Reasonable agreement between the calculated and observed cross-section values for hydrocarbons

<sup>1</sup> The survey of literature pertaining to this review was concluded in January, 1957.

<sup>2</sup> This review was written as part of work related to a research program supported by the United States Atomic Energy Commission.

were obtained for both slow electron and  $\beta$ -particle ionization. Otvos & Stevenson did observe, however, systematic differences between the relative ionization cross-sections of the nonhydrocarbons for  $\beta$ -particles and for slow electrons. These effects appear to be similar to those reported by Jesse & Sadauski (13) on the enhancement by small amounts of argon, krypton, and carbon dioxide of the ion currents produced in helium and neon by  $\alpha$ -particle bombardment. Jesse & Sadauski interpreted this effect as evidence for collisions of the second kind between foreign gas molecules and rare gas atoms in metastable states. Otvos & Stevenson also conclude that the inner electrons (which were neglected in their calculation of cross-section) play a more important role when the ionizing particles have higher initial energies.

McFadden & Wahrhaftig (14) studied the mass spectra of a series of deuterated butanes in relation to the theory of mass spectra of polyatomic molecules developed earlier by Wahrhaftig and co-workers (15) from the assumption that the mass spectra arise from the quasi-equilibrium decomposition of the parent molecule-ion through a sequence of competing unimolecular reactions. The data for *n*-butane-2-d, *n*-butane-1,1,1-d<sub>3</sub>, *n*-butane-1,1,1,3,3-d<sub>5</sub>, and *n*-butane-1,1,1,2,2,3,3-d<sub>7</sub> were interpreted with respect to isotope effect, rearrangement phenomena, and the activated complex. It was concluded that the rate of H—D exchange in the parent molecule-ion is slower than the rate of C—C bond break, but faster than the rate of loss of H<sub>2</sub> or HD. The H—D exchange apparently occurs not only between atoms on adjacent carbons but also on carbons 1-3 and 1-4. Also of interest from the radiation chemical viewpoint is the conclusion that the appearance potentials for the more abundant ions in the *n*-butane mass spectrum can be interpreted in terms of a set of reactions only if it is assumed that, in general, hydrogen atoms come off pairwise as hydrogen molecules. Independent chemical evidence for processes of this type will be considered in later sections. Bryce & Kebarle (16) in comparative studies of the mass spectra of butene and 1-butene-4-d<sub>2</sub> found that extensive migration of D atoms occurs during ionization. The latter confirms an earlier suggestion that the rearrangement of H and D atoms would be more extensive in olefinic than in paraffinic hydrocarbons [Stevenson & Wagner (17)]. This is presumably a consequence of the less localized character of the bonding in the olefinic parent molecule-ion. The authors point out that these results cast some doubt on the reliability of the "fragmentation indices" calculated by Magat & Viallard (18) to describe the probability of bond rupture in the dissociation of hydrocarbons by electron impact.

Appearance potentials for ionization processes induced by single electron impact on methanol, ethanol, and ethylacetate were measured in the mass spectrometer by Friedland & Strakna (19). The data are discussed in terms of the mechanism of quenching by polyatomic molecules in the Geiger-Müller counter. Kiser & Johnston (20) studied the decomposition of ethanol in the Geiger-Müller discharge. Decomposition of the quench gas is first order with an initial rate of  $3.5 \times 10^2$  molecules of ethanol destroyed per electron passed. These results indicate that decomposition occurs predominantly

via processes involving dissociation without ionization, i.e., by collision with electrons which have energies below that required for ionization of ethanol.

The study, by mass spectrometry, of reaction between ions and neutral molecules was continued by Schissler & Stevenson (21). In an earlier paper these authors reported preliminary cross-section data for several "onium ion" forming reactions of the type  $X^+ + YH = XH^+ + Y$  that occur in mass spectrometer ion sources. The reaction cross-sections for a large number of these proton-transfer reactions are found to be independent of temperature and inversely proportional to the average speed with which the reacting ion traverses the ion source. These characteristics permit a simple interpretation of the cross section as a specific bimolecular rate constant. When more complex molecular systems, such as lighter hydrocarbons, are involved, numerous reactions occur, and many of these result in the synthesis of carbon-carbon bonds. These processes differ from the proton transfer reactions in that (a) a negative temperature coefficient is observed, and (b) the reaction cross-section goes to zero for finite values of the average speed of the reacting ion. Although this precludes a calculation of rate constant from cross-section, the relative yield of ionic secondary-reaction product can be expressed in the usual cross-section units ( $\text{cm}^2/\text{molecule}$ ) as a function of the average energy of the reacting ion. The large magnitude that the cross-sections for such reactions as  $\text{CH}_3^+ + \text{CH}_4 = \text{C}_2\text{H}_5^+ + \text{H}_2$  acquire as the energy of the ions approach zero re-emphasizes the importance of ion-molecule reactions in radiation chemistry.

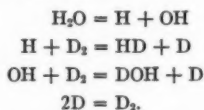
Meisels, Hamill & Williams (22) investigated the radiolysis of methane in rare gas atmospheres and found that ion-molecule reactions provide the basis for interpretation of their results. In separate experiments, a mass spectrometer was used to verify the processes (i)  $\text{CH}_4^+ + \text{CH}_4 = \text{CH}_5^+ + \text{CH}_3$ , (ii)  $\text{CH}_3^+ + \text{CH}_4 = \text{C}_2\text{H}_5^+ + \text{H}_2$ , previously reported (21) and to establish, in addition, the processes (iii)  $\text{A}^+ + \text{CH}_4 = \text{A} + \text{CH}_3^+ + \text{H}$ , (iv)  $\text{C}_2\text{H}_5^+ + \text{CH}_4 = \text{C}_3\text{H}_7^+ + \text{H}_2$ . Using 50 kv. x-rays or 1.5 Mev electrons on rare gases with added methane (e.g., A ca. 400 mm.,  $\text{CH}_4$  ca. 10 mm.) it was found that the major products are hydrogen, ethane, and propane. Small amounts of higher alkanes are also formed. Experiments with added deuterium indicate the formation of both molecular and atomic hydrogen from methane. However, with added iodine there is little  $\text{CH}_2\text{I}_2$ , indicating the  $\text{CH}_2$  radicals are not important, and that  $\text{H}_2$  is formed by an intermolecular process. The results with added iodine also demonstrate that higher alkanes, alkenes, and alkyl radicals do not have radical precursors. These facts are consistent with steps (ii), (iii), and (iv) above.

Zahlan & Burt (23) are of the opinion that ion-molecule reactions are also involved in the radiation-induced decomposition of ammonia under certain conditions of pressure and intensity. In an earlier paper, it was shown that at ammonia pressures of several hundred millimeters product formation could be interpreted on the assumption that the primary species  $\text{NH}_3^+$  and  $\text{NH}_2^+$  do not undergo reaction before neutralization. In the later paper it is stated that data obtained at higher ammonia pressures can best be explained

if the  $\text{NH}_3^+$  and  $\text{NH}_2^+$ , known to exist in irradiated ammonia, react with  $\text{NH}_3$  by proton transfer to form  $\text{NH}_4^+$ .

Dorfman (24) found in studies of HD and  $\text{D}_2$  production in the radiolysis of mixtures of deuterioethane and normal ethane, that a large fraction of the hydrogen is formed intramolecularly by direct detachment of molecular hydrogen without the apparent formation of free H atoms. In these experiments a number of mixtures of  $\text{C}_2\text{H}_6$ — $\text{C}_2\text{D}_6$  were irradiated with 1 Mev electrons, and the hydrogen fraction was analyzed mass-spectrometrically. After evaluating the contribution of secondary exchange, it was concluded that at least 50 per cent of the hydrogen is detached molecularly. Information on the effect of added iodine on product yields in this system would be of interest.

The rate of formation of HD in gaseous mixtures of tritium-water (0.284 hydrogen-atom per cent tritium) and deuterium (mole fraction  $10^{-3}$  to  $10^{-2}$ ) was studied by Firestone (25). This work may be assumed to give a direct measure of the rate of hydrogen atom formation in the radiation decomposition of water vapor by tritium  $\beta$ -particles, e.g.,



$G(\text{HD})$  is equal to  $-G(\text{D}_2)$  and corresponds to  $-G(\text{H}_2\text{O})$  according to the stoichiometry  $\text{D}_2 + \text{H}_2\text{O} = \text{HD} + \text{DOH}$ . The  $G(\text{HD})$  values average  $11 \pm 1$  molecules per 100 ev. No exchange is observed in the absence of tritium water. Absence of a dependency of  $G(\text{HD})$  on deuterium pressure indicates that  $10^{-3}$  to  $10^{-2}$  mole fraction deuterium is sufficient to remove intermediate species. Evidence against the occurrence of the possible chain  $\text{D} + \text{H}_2\text{O} = \text{H} + \text{DOH}$  is found in the fact that there is virtually no temperature coefficient for HD formation. The corresponding value determined by Hart (26) for water decomposition in liquid tritium-water containing formic acid and oxygen as free-radical scavengers gives  $-G(\text{H}_2\text{O}) = 3.8$ . The difference between  $-G(\text{H}_2\text{O})$  for liquid and vapor is interpreted as experimental evidence for a recombination reaction in liquid water ( $\text{H} + \text{OH} = \text{H}_2\text{O}$ ) in regions of the track containing high concentrations of intermediate species. Muschlitz & Bailey (27) investigated the negative ions formed from water vapor and from a mixture of water and hydrogen peroxide vapors in a mass spectrometer ion source. With water the principal ions are  $\text{H}^-$ ,  $\text{O}^-$ , and  $\text{OH}^-$ . The studies of relative ion intensities as a function of vapor pressure indicate that  $\text{OH}^-$  is not formed in a direct collision between an electron and  $\text{H}_2\text{O}$  but that a secondary over-all process such as  $\text{H}^- + \text{H}_2\text{O} = \text{OH}^- + \text{H}_2$  or  $\text{O}^- + \text{H}_2\text{O} = \text{OH}^- + \text{OH}$  takes place. These reactions have been considered by Laidler (28) in connection with the radiation chemistry of liquid water. With the addition of small amounts of hydrogen peroxide,  $\text{O}_2^-$  and  $\text{HO}_2^-$  are also formed, apparently by direct electron collision.

The production of  $\text{NO}_2$  and  $\text{NO}$  in the irradiation of  $\text{N}_2$ — $\text{O}_2$  mixtures in a nuclear reactor (BNL) was studied by Harteck & Dondes (29). Experi-

mental conditions were varied to include: compositions from 1 per cent  $N_2$ –99 per cent  $O_2$  to 99 per cent  $N_2$ –1 per cent  $O_2$ ; pressures from .01 to 50 atm.; temperatures from 193 to 300°C.; intensities from  $5 \times 10^6$  r/hr. to  $3 \times 10^8$  r/hr. Optimal yields are obtained at: a pressure of about 20 to 25 atm.; a  $N_2/O_2$  ratio approximately that of air, a temperature between 175 and 200°C.; a dose of about  $3 \times 10^8$  r/hr. or higher. Yields of  $NO_2$  and  $NO$  under these conditions are  $G(NO_2) = 6$ ,  $G(NO) = 3$ . Radiation dosage was measured by comparison with a nitrous oxide dosimeter developed by the same authors for high-level dosimetry (30).

#### ORGANIC LIQUIDS

Although the primary and intermediate processes of radiolysis can often be subjected to direct observation in gases, it is necessary in the study of condensed systems to base concepts of mechanism on more indirect evidence because of limitations imposed by track and cage effects. The fact that for organic liquids the product spectrum is usually complex, particularly for the nongaseous fractions, and difficult to analyze, has tended to retard the development of the radiation chemistry of condensed organic systems. During the past few years, however, the more general application of newer analytical methods has provided a rapidly increasing amount of information regarding the mechanism of radiation-induced reaction in these systems. A number of significant advances were made during the period under review. Through the use of gas-liquid chromatography, Dewhurst (31) made a detailed study of liquid products formed in *n*-hexane and cyclohexane liquids by irradiation with 800 kv. electrons. Irradiated *n*-hexane (dose  $8.7 \times 10^{21}$  ev/gm.) gave a chromatogram showing 16 product peaks. The tentatively identified products include *n*-pentane, 3-methyl pentane, *n*-dodecane, and a series of dodecane isomers. Seven other peaks of molecular weight intermediate between *n*-hexane and dodecane were detected but not identified. These products were found to constitute a major fraction of the total hexane decomposed. The diversity of products is indicative of a more-or-less random rupture of C—C and C—H bonds in the radiolysis of *n*-hexane. Irradiated cyclohexane (dose  $5.8 \times 10^{21}$  ev/gm.) showed only three peaks: cyclohexene ( $G = 2.3$ ), dicyclohexyl, and *n*-hexane. Dewhurst concludes that the simplicity of product formation in the radiolysis of cyclohexane must be attributed to a preferential rupture of C—H bonds, and that the ring system remains essentially intact.

The use of iodine as a scavenger in the study of mechanism in hydrocarbon radiolysis has been extended by Schuler (32) to include liquid benzene. In previous work (33), it was shown that the disappearance of iodine at an initial concentration of  $10^{-4}$  *M* in irradiated hydrocarbon solutions is due to reaction with organic radicals and not to reaction with hydrogen atoms. Hydrogen yields from aliphatic hydrocarbons were found not to be appreciably affected by iodine at the same concentrations which are effective in removing organic free radicals. The more recent study indicates that a similar situation exists in the  $\gamma$ -radiolysis of benzene in that the hydrogen yield  $G(H_2) \approx 0.036$  is essentially the same for pure benzene and for benzene con-

taining .02 to .04 *M* iodine. For dilute solutions of iodine in benzene the *G* for iodine disappearance is about 0.35. Since iodine is expected to be a good scavenger for both H atoms and organic free radicals, it is concluded that hydrogen production occurs almost entirely by processes that form hydrogen in a single step, possibly by an ultimate molecule mode of decomposition.

Closely related to the above studies is the additional information on mechanism in the x-ray-induced radiolysis of the liquid alkyl iodides which has been obtained by Schuler & Petry (34). The predominant decomposition products of liquid ethyl iodide, *n*-propyl iodide, and isopropyl iodide are iodine and hydrocarbons of the same carbon number as the parent compound. With isopropyl iodide, for example, the following product *G* values are obtained: I<sub>2</sub>, 2.65; C<sub>3</sub>H<sub>6</sub>, 2.25; C<sub>3</sub>H<sub>8</sub>, 1.89; C<sub>2</sub>H<sub>2</sub>, 0.0; C<sub>2</sub>H<sub>4</sub>, 0.004; CH<sub>4</sub>, 0.01; H<sub>2</sub>, 0.26. Yields are proportional to dose over a wide range. The absence of an appreciable induction period in these systems indicates (a) that the first trace of iodine produced by the initial reaction is sufficient to quench all homogeneously distributed thermal radicals via  $R + I_2 = RI + I$ , and (b) that the observed products are formed exclusively by processes other than those involving homogeneously distributed thermal radicals, i.e., by hot reactions, by reactions of excited or ionic species, or both, and by processes occurring at the high radical concentrations present in the track. The fact that added radioiodine scavenger is recovered in organic combination almost exclusively as the parent species shows that the production of thermal radicals occurs preferentially through rupture of the C—I bond. When dissolved oxygen is present, the rate of iodine production is increased as a result of the competition of the reaction  $R + O_2 = RO_2$  with  $R + I_2 = RI + I$ .

The processes initiated by the reaction of oxygen with labile intermediates formed in the radiolysis of organic liquids have received relatively little attention, although the use of oxygen as a scavenger would appear to offer an interesting approach to the study of the primary processes. Most of the literature in this particular field is related more directly to the problems associated with the practical utilization of high energy radiation. The recent work of Lang & Proctor (35) and that of Dugan & Landis (36) involves studies of the effect of oxygen in peroxide and carbonyl formation in the irradiation of lipids and related fatty acids. The series of papers by Bach and co-workers (37) provide information on oxygen as a scavenger in the x-radiolysis of a number of simpler organic liquids including *n*-heptane, *iso*-octane, cyclohexane, toluene, and benzene. In general, it appears for liquid hydrocarbons that the principal liquid products are di-substituted peroxides, hydroperoxides, carbonyls, and acids. Comparison of these yields with those for iodine disappearance in the same system [cf. (33)] is of interest in that the rate constants for the reactions  $R + O_2$  and  $R + I_2$  are estimated to be about equal in magnitude [see Willard (11, p. 613)]. From this viewpoint, the low hydrogen peroxide yields appear to be consistent with the conclusion arrived at in the iodine studies, namely, that organic radicals and not hydrogen atoms are available for reaction with added solute. The data of Bach *et al.* also show, as have other comparative studies, that the organic radical yield



in benzene is considerably lower than in the liquid alkanes. Linear dose-yield dependencies were obtained in the initial production of organic peroxide, carbonyl, and acid functional groups. A number of parallel reaction paths are postulated in terms of possible reactions with oxygen of alkene radicals, alkylidene diradicals, and excited molecules. The interesting suggestion is made that the reaction of alkylidene diradicals with oxygen followed by rearrangement, e.g.,  $\text{RCH} + \text{O}_2 = \text{RCOOH}$  may account for the linear dose-yield relationship of the organic acid fraction. Bach and co-workers also studied the x-ray radiolysis of acetic acid and ethyl alcohol under both oxygen-free and oxygen-saturated conditions. The oxygen effect in acetic acid is similar to that observed with hydrocarbons in that hydrogen peroxide is a minor product. Oxygen does not change the carbon dioxide yield value [cf. Garrison *et al.* (38)].

In the radiolysis of liquid primary alcohols formation of the major products: hydrogen, aldehyde, and vicinal glycol apparently involves intermediate processes which introduce H atoms as well as organic free radicals into the bulk of the solution. In an extension of earlier work, Newton & McDonell (39) found in studies of helium ion irradiation of liquid ethyl alcohol that radiation yields for hydrogen, total carbonyl, and vicinal glycol decrease markedly with increasing dose over the range .029 to  $2.7 \times 10^{22}$  ev/ml. In studying the mechanism of the "protective" action of the products it was found that added acetaldehyde or hexene-1 at concentrations of approximately 1 per cent were effective in decreasing the hydrogen yield. In the latter case, *n*-hexene was found as an additional product. These results suggest that at least part of the hydrogen produced in the radiolysis of liquid ethanol is formed through reactions of thermalized H atoms. A similar conclusion regarding hydrogen production in the case of methyl alcohol was reached by McDonell & Gordon (40) in interpreting their observation that values for the yield-ratio ethylene glycol/formaldehyde are considerably greater with  $\text{Co}^{60}$   $\gamma$ -radiation than with more densely ionizing helium ions. Data on the effect of oxygen on the radiation yields of aldehydes and glycols from alcohols would be of interest. Bach *et al.* (37) reported that the yield of aldehyde from oxygen-saturated ethanol under x-ray irradiation is approximately four times that obtained under the corresponding oxygen-free condition but made no mention of the glycol fraction. A radiation-induced chain oxidation is apparently involved.

Burr (41), in work done as a preliminary to the study of radiation effects in tracer-labeled ethanol, found no radiation-induced H exchange between molecular hydrogen and the alcohol molecule.

The study of energy transfer processes in the radiolysis of liquid organic mixtures has been continued by Burton and co-workers (42). The quenching effect of oxygen and of bromobenzene on the  $\text{Co}^{60}$   $\gamma$ -induced luminescence of *p*-terphenyl in benzene, in cyclohexane, and in toluene; of *m*-terphenyl in benzene and in cyclohexane; and of 1,4-diphenylbutadiene in benzene, and in cyclohexane have been investigated. The results are interpreted on the basis of electronic energy transfer (via emission of virtual photons) from ex-



cited solvent molecules to scintillator molecules. The quenching of luminescence is shown to be almost completely attributable to an interaction between the quencher and the excited solvent. The efficiency of quenching remains constant with increasing bromobenzene concentration up to  $\approx 0.1 M$ . However, for oxygen, the quenching efficiency shows an increase with increasing concentration. It is of interest in this regard to note that Evans (43) has obtained evidence which suggests that the quenching effect of oxygen (and nitric oxide) on the fluorescence of aromatic hydrocarbons may be due to a magnetic perturbation which facilitates the excited singlet-triplet radiationless transition. The triplet level of bromobenzene is already considerably perturbed by the heavy bromine atom, and very little change in the well-defined triplet absorption band is observed on saturation with oxygen.

The radiation-induced polymerization of liquid vinyl monomers received considerable attention during the past year, not only from the radiation chemical viewpoint, but also from the standpoint of its application to the general study of polymerization phenomena. Ballantine *et al.* (44) calculated G values for the rate of the  $\text{Co}^{60}$   $\gamma$ -ray initiation of polymerization in styrene and methyl methacrylate monomers over the temperature range  $-18$  to  $72^\circ\text{C}$ . Rate values were calculated on the basis of the relationship derived by Tobolsky and co-workers (45) for systems in which the initial radical concentration is uniform. That the condition of uniform radical concentration is valid for the case of  $\gamma$ -ray initiation was established in studies of the relationship between rate of polymerization and radiation intensity, i.e., a dependence of polymerization rate on  $I^{0.5}$  was found for both styrene and methyl methacrylate up to intensities of  $3 \times 10^5$  rep/hr. The calculated G values for initiation at  $25^\circ\text{C}$ . are 2.08 and 36.0 for styrene and methyl methacrylate respectively. These results are in close agreement with those reported by Prévot-Bernas *et al.* (46) who used diphenylpicrylhydrazyl (DPPH) to determine rates of  $\gamma$ -ray initiation. The G values obtained by Seitzer & Tobolsky (47) for  $\text{Sr}^{90}$ — $\text{Y}^{90}$   $\beta$ -ray initiation are lower by a factor of approximately 10, although the ratios of G values are consistent among the three groups. The fact that the initial nonuniform radical distribution obtained in  $\gamma$ -ray initiation does not disturb the  $I^{0.5}$  dependency, and can therefore be treated in terms applicable to systems of uniform concentration, indicates that the chains are of long life, and that the chain carriers have in effect a high coefficient of diffusion [Collinson & Dainton (48)]. Bouby *et al.* (49) also point out that the  $I^{0.5}$  dependency is apparently characteristic of  $\gamma$ -ray-induced polymerizations in which the polymer is soluble in the monomer as is the case with styrene and methyl methacrylate. For polymerization in a precipitating medium the rate of polymerization over a range of intensities is proportional to  $I^n$  where  $0.5 < n < 1.0$ . The formation of vinyl chloride and acrylonitrile polymers in pure monomer is representative of the latter case. Bensasson & Prévot-Bernas (50) found  $n > 0.5$  for the  $\text{Co}^{60}$   $\gamma$ -ray-induced polymerization of acrylonitrile monomer. Chapiro (51) obtained a similar result in the  $\gamma$ -ray-induced polymerization of vinyl chloride monomer. These

authors conclude that the departure from the  $I^{0.5}$  dependency which is observed with these substances cannot be attributed to nonuniform kinetics, but is related to the fact that the polymer precipitates from the medium. It is pointed out that a value for  $n > 0.5$  is also obtained in the polymerization of certain vinyl monomers by chemical catalysts.

The radiation stability of organic compounds as reactor moderator-coolants has been discussed by Bolt & Carroll (52), Colichman & Gercke (53), and by Freund (54).

#### ORGANIC SOLIDS

Miller, Lawton & Balwit (55) reported a detailed study of the radiation chemistry of the solid hydrocarbons: polyethylene, polymethylene, and octacosane. Irradiations were made with 800 kv. electrons; cross-linking, gas evolution, and changes in unsaturation were determined. The only type of unsaturation formed is *trans*-vinylene, and this is formed in approximately the same yield with all three hydrocarbons. In agreement with the observations of Dole *et al.* (56), it was found that the vinyl ( $-\text{CH}=\text{CH}_2$ ) and vinylidene ( $>\text{C}=\text{CH}_2$ ) unsaturation initially present in polyethylene disappear at approximately 15 and 50 megaroentgen, respectively. It is concluded, however, that although the initial unsaturation probably contributes to the cross-linking of polyethylene in the early stages of irradiation it is not a prerequisite for the cross-linking reaction. It is concluded also that cross-linking and the formation of *trans*-vinylene unsaturation are independent processes. The former is interpreted on the basis of an initial C—H bond rupture followed by hydrogen abstraction from an adjacent chain to give  $\text{H}_2$  and two polymer radicals in a favorable position for cross-linking. Vinylenes formation is assumed to involve a reaction in which  $\text{H}_2$  is formed from adjacent H atoms on the same chain. In view of the fact that with liquid hydrocarbons there is little effect of iodine scavenger on hydrogen yields (33), it seems unlikely that either of the described processes involve thermalized H atoms. Pearson (57) has made the interesting suggestion that the formation of *trans*-vinylene groups, rather than being an alternate to cross-linking, may be an intermediate step in the cross-linking process. The author points out, on the basis of a survey of published experimental data from various sources, that the formation of *trans*-vinylene unsaturation in irradiated polyethylene apparently approaches a maximum at high doses. The maximum suggests that a radiation-induced reaction leads to an equilibrium value of vinylenes groups. Since hydrogen evolution does not decrease, this reaction is not the resaturation of vinylenes groups by evolved hydrogen. The mechanism proposed by Pearson involves the sequence  $\text{RH} = \text{R} \cdot + \text{H}$ ,  $\text{H} + \text{RH} = \text{R} \cdot + \text{H}_2$ , followed by disproportionation of radical sites R to give *trans*-vinylene unsaturation. Cross-linking then occurs through addition of  $\text{R} \cdot$  to *trans*-vinylene as the latter increases with irradiation. Application of stationary state kinetics to the reaction sequence shows that the hydrogen evolution would be linear, and that vinylenes unsaturation would approach a limiting value [cf. Dole *et al.* (56)]. Other more general aspects of the kinetics of radiation-induced reaction in

polyethylene have been treated mathematically by Okamoto & Ishihara (58). Black (59) measured the effect of temperature upon the cross-linking of polyethylene by  $\text{Co}^{60}$   $\gamma$ -ray irradiation over the temperature range  $77^\circ$  to  $348^\circ\text{K}$ . The cross-linking yields  $G(\text{C})$  were derived from measurements of the elastic modulus. As with polymers in which degradation predominates [A. Charlesby (60)] less energy is required to produce a cross-link in polyethylene as the temperature is increased. A plot of  $\log G(\text{C})$  against  $1/T$  gave an approximately linear relationship down to  $-80^\circ\text{C}$ . [cf. Lawton, Bueche & Balwit (61)].

An investigation of the theory of rubber elasticity using irradiated polydimethylsiloxanes was made by Bueche (62). Irradiations were made with 800 kvp electrons. Equilibrium tension measurements at low elongations were used to determine the number of chains between cross links as given by the kinetic theory of elasticity. The dependence of the number-average molecular weight of irradiated polydimethylsiloxane fluids on radiation dose was determined. These data were analyzed to find the efficiency of cross-link formation in the polymer. It is significant that the number of chains between cross links produced by a given dose and determined by the kinetic theory was found to be only one-half the number to be expected from the measurement of the molecular weights of the irradiated fluids. No explanation for this difference was offered. It would seem, however, that non-uniform cross linking along a particle track could be a contributing factor. Further investigation of this effect would be of interest. Data on the elastic modulus, tensile strength, and other properties of  $\gamma$ -irradiated rubber were obtained by Gehman & Auerbach (63).

Further studies have been made of the action of ionizing radiation on polymers in which degradation rather than cross-linking reactions predominate. The fact that degradation is the major effect in polymers which do not contain at least one hydrogen atom in the  $\alpha$ -position to the  $-\text{CH}_2-$  group, e.g., polymethylmethacrylate, polyisobutylene, cellulose acetate [Miller *et al.* (64)], has been interpreted by Chapiro (65, 66) in terms of multiple bond-rupture processes that are similar to those considered by Magat & Viallard (67) in their discussion of the mass spectra of hydrocarbons containing a quaternary carbon atom. Henglein & Boysen (68) have made the interesting observation that stable, macromolecular, free *N*-poly-radicals are formed in the  $\gamma$ -ray irradiations of oxygen-free polymethylmethacrylate, polystyrene, and polyvinyl acetate containing dissolved diphenylpicrylhydrazyl.

The  $\gamma$ -ray initiated polymerization of crystalline monomers has been investigated further by Mesrobian and co-workers (69). Polymerization was found to be initiated in acrylamide, methacrylamide, methylene-bis-acrylamide, vinyl carbazole, vinyl stearate, acrylic acid, methacrylic acid, and potassium, calcium, and barium acrylates, but was not observed in crystalline maleic anhydride, allylamine hydrochloride and picrate, and stilbene. It is pointed out that the observed apparent first-order relationship between polymerization of acrylamide and irradiation intensity up to  $3 \times 10^6$  rep/hr. indicates that polymerization of this compound proceeds in discrete tracks.

The constancy of molecular weight over a 270-fold intensity range is also consistent with a nonhomogeneous reaction. Polymerization data obtained with the acrylic acid salts are interpreted as indicating that lattice defects or spur spacings determine the kinetic chain length whenever the heat of polymerization is insufficient to disrupt the lattice order. Lawton, Grubb & Balwit (70) found that polymerization of hexamethylcyclotrisiloxane in the solid state is initiated by 800 kv. electron irradiation. The polymerization rate decreased abruptly to nearly zero above the melting point (64°C.). Possible effects of spatial orientation are discussed.

The use of microwave magnetic resonance in the study of radiation effects in solid organic materials was extended by Gordy and associates (71, 72) to include some simple alcohols, amines, amides, mercaptans and the methyl and ethyl compounds of zinc, mercury, and tin. The samples were irradiated (40 kv. x-rays) and studied at 77°K. The proton hyperfine structure of the electron spin resonance permitted fairly definite identification of some radical species. Methyl alcohol, acetamide and sodium methoxide appeared to form the radical  $(CH_2)^+$ . Ethyl alcohol and propionamide gave resonance attributable to  $(C_2H_4)^+$ . The  $(C_2H_4^+)$  radical is also believed to be produced from mercury dimethyl,  $C_2H_6$  from mercury diethyl and  $CH_3$  from zinc dimethyl. Monfils and co-workers reported further studies of the effects of  $\gamma$ -ray irradiation on *p*-dichlorobenzene (73) and  $\gamma$ -hexachlorocyclohexane (74) as measured by changes in the nuclear quadrupole resonance of the irradiated solid.

Recent work by Pollard and associates on the inactivation of biologically active material by charged-particle bombardment includes studies of: the radiation sensitive volume of adrenocorticotrophic hormone (ACTH) by deuteron bombardment (75), the inactivation with fast charged particles of infectivity and hemagglutination in influenza A virus (76), the cross reaction of deuteron bombarded T 1 bacteriophage (77). Also of interest in conjunction with radiation chemical studies of biological materials in the solid state are the following: Grossweiner (78) on the metastable states of photo-excited ovalbumin and constituents, Shore & Pardee (79) on the energy transfer in conjugated proteins and nucleic acids, and Preiss & Setlow (80) on the spectra of amino acids, peptides, nucleic acids, and protein in the vacuum ultraviolet.

#### WATER AND AQUEOUS SOLUTIONS

The numerous studies of radiation-induced oxidation-reduction reactions in aqueous solutions are consistent with the view that (a) the earliest detectable products of the ionization and excitation processes induced in water by radiation absorption are hydrogen atoms, hydroxyl radicals, hydrogen, and hydrogen peroxide, (b) light-particle radiation yields predominantly free radicals, whereas heavy-particle radiations yield principally hydrogen, and hydrogen peroxide, and (c) the number of water molecules decomposed per 100 ev of absorbed energy is in the neighborhood of 4, independent, to a first approximation, of the particular type of radiation. The formation of molecular products is generally believed to result from the pairwise combination

of H and OH radicals formed in regions of high density of energy release along the track of the charged particles. The free-radical yield is considered to represent that fraction of the total radical production which escapes during expansion of the track.

The theoretical treatment of track effects has been extended by Ganguly & Magee (81) to include a model for dissipation of the tracks of high-energy particles. It is assumed that all radicals are formed close to the spur sites of original ionizations [(i)  $\text{H}_2\text{O} = \text{H}_2\text{O}^+ + e$ , (ii)  $\text{H}_2\text{O}^+ + e = \text{H} + \text{OH}$ ] or highly energetic excitations [ $\text{H}_2\text{O} = \text{H} + \text{OH}$ ]. The track is taken as a series of spurs randomly spaced along the trajectory of the particle. A Gaussian distribution for the position of the radicals in a spur is assumed, and all spurs are assumed to have the same number of radicals. The competition of radical-radical, and radical-solute reactions in a track expanding by diffusion is treated. An interesting result is that an effect is calculated for the intermingling of radicals from adjacent spurs even for lightly ionizing particles, such as electrons, having energies of approximately 1 Mev. Further refinement of the model would be expected to involve a consideration of the distribution of spur sizes.

Although ionic and free-radical species involved in the radiation decomposition of water have lifetimes which are too short to permit their direct observation in liquid systems, some of these entities reach concentrations high enough for physical and chemical detection in irradiated ice at low temperatures. The initial geometrical distribution of energy in spurs along the particle tracks may be assumed to be about the same in ice as in liquid water. Ghormley & Stewart (82) have studied the effects of  $\gamma$ -radiation on ice at temperatures down to  $-269^\circ$ . At  $-196^\circ$  and below, dissolved hydrogen or oxygen molecules do not enter into reactions which appreciably affect the final concentration of hydrogen peroxide. At higher temperatures, reactions involving solutes at low concentration are observed. The high yields for radiation-induced reaction between hydrogen and hydrogen peroxide above  $-50^\circ$  suggest the possibility of a chain reaction such as has been postulated for liquid water: (i)  $\text{H}_2\text{O}_2 + \text{H} = \text{H}_2\text{O} + \text{OH}$ ; (ii)  $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$ . The upper limit of the temperature range in which hydrogen peroxide disappears following irradiation at  $-196^\circ$  corresponds, within experimental error, to the temperature ( $-158 \pm 10^\circ$ ) observed by Matheson & Smaller (83) for annealing of paramagnetic species (H atoms) in irradiated ice. Ghormley (84) has also made thermoluminescence measurements on ice irradiated at  $-196^\circ \text{C}$ . with  $\text{Co}^{60}$   $\gamma$ -rays. Heating at a rate of  $10^\circ \text{C./min.}$  after an irradiation of  $10^{18}$  ev/gm gave glow curves similar to those previously reported (85) with the predominant peak at  $-115^\circ$ . However, after an irradiation of  $10^{21}$  ev/gm, the predominant peak appeared at  $-155^\circ$  and had 100 times the intensity of the  $-115^\circ$  peak. The emission at  $-155^\circ$  was found to be 90 per cent ultraviolet, while emission at  $-115^\circ$  was nearly all in the visible range. The process which results in the glow curve at  $-155^\circ$  has the same temperature dependence as the predominant process which results in the disappearance of  $\text{H}_2\text{O}_2$  after irradiation of ice at  $-196^\circ$ .

A number of papers have treated other aspects of intermediate processes

involved in the radiolysis of aqueous solutions. Weiss (86) has suggested that the  $\text{H}_2\text{O}^+$  ion generally assumed to be a short-lived intermediate in water radiolysis, may have some stability in liquid water, and that the equilibrium  $\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}$  may have a bearing on the pH dependency of certain reactions attributed to the OH radical. It is also suggested that in acid solution hydrogen peroxide formation may involve the reactions (i)  $\text{H}_2\text{O}^+ + \text{OH} = \text{H}_3\text{O}_2^+$  (ii)  $\text{H}_3\text{O}_2^+ \rightleftharpoons \text{H}_2\text{O}_2 + \text{H}^+$ , and that, in general, for all OH reactions in aqueous solution, processes involving participation of  $\text{H}_3\text{O}_2^+$  radical may have to be taken into account. Coulson (87) presented a qualitative theoretical discussion of the stability in liquid water of the ionic intermediates  $\text{H}_2^+$  and  $\text{OH}^+$  proposed by Weiss (88) and Dainton (89) respectively. Since the original suggestion by Weiss, it has been recognized that H radicals in acid solution may participate in oxidation reactions through formation of  $\text{H}_2^+$  by the reaction  $\text{H} + \text{H}^+ \rightleftharpoons \text{H}_2^+$ . Coulson concludes that such stability that hydrated  $\text{OH}^+$  might possess is distinctly less than that of hydrated  $\text{H}_2^+$ . Lefort & Douzou (90) have concluded that their studies of the photochemical oxidation of aqueous ferrous ion at different pH values do not require the concept of  $\text{H}_2^+$  for interpretation.

Haissinsky (91), on the basis of a review of the radiation chemistry of aqueous solutions containing dissolved oxygen, has proposed that the participation of molecular oxygen in radiation-induced reactions in aqueous systems generally depends on a preliminary formation of the  $\text{O}_2^-$  ion. Haissinsky & Pujo (92) have observed that the presence of barium sulfate or metallic silver increases the G value for silver reduction in irradiated silver nitrate solution, and attribute this to a catalytic effect of the solid phase. Ghormley (93), using a pulsed 1.4 Mev electron beam from a Van de Graff generator, has estimated that the lifetime of the shortest-lived intermediate whose concentration affects the steady state hydrogen peroxide concentration in liquid water is about  $10^{-8}$  sec. as determined at beam currents in the microampere range. The lifetime would be expected to increase with decreasing radiation intensity.

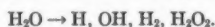
Quantitative yield studies of radiation chemical change in dilute aqueous solutions have shown that a complete representation of the radiation decomposition of water requires three separate stoichiometric relationships [Dainton & Sutton (94); Allen (95)]. These are generally written (95):



The yields of R, F, E have been measured in a large number of dilute solutions, and, to a first approximation, are fairly constant for a particular radiation. For recent summaries see Lind & Hochanadel (1); Collinson (96). However, it has been shown that the primary yields can be influenced appreciably by certain solutes even at low concentration [Sworski (97); Allen & Holroyd (98)], and are somewhat pH dependent [Hart (99)]. Since the yields of R, F,



E are not invariant, it has become more convenient to represent the primary radiation process in water by the combined expression (1,100):



The only implied stoichiometry is that required by the over-all reaction, i.e.,  $2\text{G}_\text{P}(\text{H}_2) + \text{G}_\text{P}(\text{H}) = 2\text{G}_\text{P}(\text{H}_2\text{O}_2) + \text{G}_\text{P}(\text{OH})$ , where  $\text{G}_\text{P}$  refers to the earliest detectable yield of the specific product from water. This notation and those of Allen and Hart have the equivalencies shown below. In Hart's notation, reactions 1, 2, 3 correspond to reactions R, F, E of Allen:

$\text{G}_\text{P}(\text{H})$	$\text{G}(1) + \text{G}(3)$	$\text{G}_\text{R} + \text{G}_\text{E}(\text{H})$
$\text{G}_\text{P}(\text{OH})$	$\text{G}(1)$	$\text{G}_\text{R}$
$\text{G}_\text{P}(\text{H}_2)$	$\frac{1}{2}\text{G}(2)$	$\text{G}_\text{F}$
$\text{G}_\text{P}(\text{H}_2\text{O}_2)$	$\frac{1}{2}\text{G}(2) + \frac{1}{2}\text{G}(3)$	$\text{G}_\text{F} + \text{G}_\text{E}(\text{H}_2\text{O}_2)$

The notations referred to in later sections of this review may be inferred from the symbols employed, and unless stated otherwise, correspond to those used in the original article.

The recent work of Donaldson & Miller (101) which confirms and extends the earlier observations of Hart (102) indicates that the  $\text{HO}_2$  radical, in addition to H and OH, also may be considered a primary product. The evidence for this proposal is derived from radiation chemical studies of the ferrous sulfate-cupric sulfate actinometer. Hart found in the  $\gamma$ -ray irradiation of oxygen-free solutions containing ferrous and cupric ions that the primary products of water decomposition H, OH, and  $\text{H}_2\text{O}_2$  are readily removed via: (i)  $\text{Cu}^{+2} + \text{H} = \text{Cu}^+ + \text{H}^+$  (ii)  $\text{Fe}^{+2} + \text{OH} = \text{Fe}^{+3} + \text{OH}^-$  (iii)  $\text{Fe}^{+2} + \text{H}_2\text{O}_2 = \text{Fe}^{+3} + \text{OH}^- + \text{OH}$ . However, molecular oxygen was also observed in small but definite yield. From a consideration of several factors it was concluded (a) that the evolved oxygen was not produced in a direct primary process but was formed by the reaction  $\text{Cu}^{+2} + \text{HO}_2 = \text{Cu}^+ + \text{H}^+ + \text{O}_2$  and (b) that the  $\text{HO}_2$  involved in this reaction was produced in the track volume via  $\text{OH} + \text{H}_2\text{O}_2 = \text{HO}_2 + \text{H}_2\text{O}$ . In the absence of cupric ion, the  $\text{HO}_2$  disappears via  $\text{Fe}^{+2} + \text{HO}_2 = \text{Fe}^{+3} + \text{HO}_2^-$ . Donaldson & Miller extended these observations in a comprehensive study of the same system under irradiation with  $\text{Po}^{210}$   $\alpha$ -particles. They concluded that the only explanation consistent with all the experimental facts is that previously suggested, viz. reaction between OH and  $\text{H}_2\text{O}_2$  occurs during the expansion of the track and the  $\text{HO}_2$  which is formed reacts with either  $\text{Cu}^{+2}$  or  $\text{Fe}^{+2}$ , depending on the pH of the solution and on the ratio  $(\text{Cu}^{+2})/(\text{Fe}^{+2})$ . The authors point out that if the proposed interpretation is correct,  $\text{HO}_2$  could be considered a primary product of irradiation with  $\text{G}(\text{HO}_2)$  being equal to  $\text{G}(\text{O}_2)$ . It is also suggested that the notation of Dewhurst & Burton (100) is more appropriate for the inclusion of  $\text{HO}_2$  as a primary species. Approximate yields of the primary products of  $\alpha$ -particle irradiation for solutions .01 N to 1 N in sulfuric acid are given as:  $\text{G}_\text{P}(\text{H}) = 0.77$ ,  $\text{G}_\text{P}(\text{HO}_2) = 0.25$ ,  $\text{G}_\text{P}(\text{OH}) + 2\text{G}_\text{P}(\text{H}_2\text{O}_2) = 3.12$ ,  $\text{G}_\text{P}(\text{H}_2) = 1.55$ , and  $-\text{G}(\text{H}_2\text{O}) = 3.62$ .

Yields for water decomposition by deuteron and proton irradiation as a



function of particle energy have been obtained by Hart, Ramler & Rocklin (103) from  $G(\text{Fe}^{+3})$  measurements in oxygen-aerated ferrous sulfate and ferrous sulfate-cupric sulfate solutions. In the former dosimeter the free radical plus molecular hydrogen peroxide yields are measured, whereas in the latter dosimeter only hydrogen peroxide formed in equimolar amounts with hydrogen is measured [Hart (102)]. The following approximate relationships are obtained:  $G(\text{Fe}^{+3}) = 4[G(1) + G(3)] + G(2)$ ;  $G(\text{Fe}^{+3} - \text{Cu}^{+2}) = G(2)$ . Two approximations are involved: (a) the yields of the primary reactions 1, 2, and 3 are independent of pH in the range 0.4 to 2.1; and (b) the products or reactions liberating molecular oxygen are negligible. The calculated values of  $G(\text{H}_2\text{O})$  range (a) from 3.48 to 3.08 as the deuteron energy is decreased from 21.24 Mev to 3.35 Mev and (b) from 3.18 to 3.73 as the proton energy is decreased from 1.99 Mev to 0.29 Mev [the corresponding value for  $\text{Co}^{60}$   $\gamma$ -rays as measured with the same dosimeters is 4.47]. The data are also calculated in terms of the number of water molecules decomposed per 100 ev of energy dissipated locally along the track. A plot of this value,  $G_1$ , as a function of the corresponding track distance,  $D_1$ , indicates that fewer molecules are decomposed for low  $D_1$  (high ionization density) than for high  $D_1$ . This is also supported by the  $\gamma$ -ray results.

Garrison, Weeks & Ward (104), using the formic acid-oxygen dosimeter [Hart (99)] obtained the values  $G(1) = 2.39$ ,  $G(2) = 1.26$  for 10 Mev protons. With this dosimeter at pH values above 3;  $G(\text{H}_2\text{O}_2) = G(1) + \frac{1}{2}G(2)$ ;  $G(\text{CO}_2) = G(1)$ ;  $G(3) = 0$  to a first approximation. With the spectrum of fast neutrons obtained by bombardment of beryllium with 24 Mev deuterons, a value of 0.85 was obtained for the ratio  $G(1)/[G(1) + \frac{1}{2}G(2)]$ . Ebert, Howard-Flanders & Moore (105) found that with the neutron spectrum produced by bombardment of beryllium with 2 Mev deuterons, the influence of oxygen on hydrogen peroxide yields in neutral water is comparable to that obtained with  $\alpha$ -rays.

There seems to be general agreement regarding the yields of intermediates in the radiolysis of water by  $\gamma$ -rays, x-rays, or fast electrons. Hochanadel & Lind (1), on the basis of a critical survey of published data, conclude that the most representative values ( $10^{-2}$   $N$   $\text{H}_2\text{SO}_4$  to neutral solution) are  $G_P(\text{H}_2) = 0.45$ ,  $G_P(\text{H}_2\text{O}_2) = 0.80$ ,  $G_P(\text{H}) = 2.75$ ,  $G_P(\text{OH}) = 2.05$ . Although most workers have obtained values of  $[G_P(\text{H}) + G_P(\text{OH})]/2$  in the neighborhood of 3 for these radiations, an interesting exception has been the value  $9.84 \pm 1.40$  (based on a value of  $G(\text{Fe}^{+3}) = 15.5$  for the ferrous sulfate dosimeter) obtained several years ago by Dainton & Rowbottom (106) from comparative studies of the decomposition of aqueous hydrogen peroxide by  $\text{Co}^{60}$   $\gamma$ -rays and by 3660 Å light. The results were based on a value of 1.0 for the primary quantum yield of hydrogen peroxide dissociation at 2537 Å and the assumption that the quantum yield at 2537 Å and 3660 Å are the same. As noted by Dainton & Rowbottom, their value would be reduced if the primary quantum yield of  $\text{H}_2\text{O}_2$  decomposition is less than 1. Weeks & Matheson (107) redetermined the primary quantum yield for hydrogen peroxide dissociation at 2537 Å in photolysis studies of aqueous

hydrogen peroxide-formic acid solutions containing oxygen and obtained the value  $0.49 \pm 0.065$ . Dainton (108) also reinvestigated this problem in studies of the kinetics of the polymerization of acrylamide in deaerated aqueous solutions initiated (a) by  $\gamma$ -rays and (b) by 3130 Å light. These data are consistent only if the primary quantum yield for hydrogen peroxide photolysis in aqueous solutions at 3130 Å has the value 0.30. The anomaly introduced by the earlier data of Dainton and Rowbottom appears to have been largely resolved.

Sworski (109) extended previous studies of the  $\text{Co}^{60}$   $\gamma$ -ray-induced decomposition of water in 0.8 *N* sulfuric acid solutions containing ceric and thalious ions. The radiation-induced reduction of  $\text{Ce}^{+4}$  in the absence of  $\text{Ti}^{+3}$  conforms to: (i)  $\text{H} + \text{Ce}^{+4} = \text{Ce}^{+3} + \text{H}^+$ , (ii)  $\text{OH} + \text{Ce}^{+3} = \text{Ce}^{+4} + \text{OH}^-$ , (iii)  $\text{H}_2\text{O}_2 + 2\text{Ce}^{+4} = 2\text{Ce}^{+3} + 2\text{H}^+ + \text{O}_2$ , with  $G(\text{Ce}^{+3})$  equal to  $2G_{\text{P}}(\text{H}_2\text{O}_2) + G_{\text{P}}(\text{H}) - G_{\text{P}}(\text{OH})$ . In solutions containing both  $\text{Ce}^{+4}$  and  $\text{Ti}^{+3}$  it is shown that  $G(\text{Ce}^{+3}) = 2G_{\text{P}}(\text{H}_2\text{O}_2) + G_{\text{P}}(\text{H}) + G_{\text{P}}(\text{OH})$ . The effect of  $\text{Ti}^{+3}$  is consistent with the assumption that OH radicals which normally oxidize  $\text{Ce}^{+3}$  to  $\text{Ce}^{+4}$  are removed by the reaction  $\text{OH} + \text{Ti}^{+3} = \text{OH}^- + \text{Ti}^{+2}$ . The postulated intermediate,  $\text{Ti}^{+2}$ , in turn, reduces  $\text{Ce}^{+4}$  to  $\text{Ce}^{+3}$  with concomitant formation of  $\text{Ti}^{+3}$ .  $G(\text{Ti}^{+3})$  is thus equal to  $G(\text{OH})$ . The reported yield values  $G_{\text{P}}(\text{H}) = 3.70$ ,  $G_{\text{P}}(\text{OH}) = 2.92$ ,  $G(\text{H}_2) = 0.39$ , and  $G_{\text{P}}(\text{H}_2\text{O}_2) = 0.78$  are consistent with the proposed overall mechanism. Sworski (110) also measured relative rate values for reaction of OH radicals with sulfuric acid, cerous ion, and formic acid in radiolysis studies of ceric ion-cerous ion-formic acid mixtures in 0.4 *M* sulfuric acid.  $G(\text{Ce}^{+3})$  increases with decreasing  $(\text{Ce}^{+3})/(\text{HCOOH})$  ratio at any constant cerous ion concentration while at constant  $(\text{Ce}^{+3})/(\text{HCOOH})$  ratio  $G(\text{Ce}^{+3})$  decreases with decreasing total concentration of cerous ion and formic acid. A quantitative interpretation of the data, assuming that the three solutes compete for OH according to (i)  $\text{Ce}^{+3} + \text{OH} = \text{Ce}^{+4} + \text{OH}^-$ , (ii)  $\text{HCOOH} + \text{OH} = \text{HCOO} + \text{H}_2\text{O}$ , (iii)  $\text{H}_2\text{SO}_4 + \text{OH} = \text{HSO}_4 + \text{H}_2\text{O}$ , gave the values 1.70, 380, 650 for the ratios  $k_{\text{i}}/k_{\text{ii}}$ ,  $k_{\text{ii}}/k_{\text{iii}}$ ,  $k_{\text{i}}/k_{\text{iii}}$  respectively.

Challenger & Masters (111) found that the x-ray-induced  $\text{Ti}^{+3}$ - $\text{Ti}^{+4}$  exchange can be interpreted on the basis of the formation of the intermediate species  $\text{Ti}^{+2}$  at appreciable steady state concentrations. The radiation-induced exchange rate was independent of  $(\text{Ti}^{+3})$ , .50-order-dependent on  $(\text{Ti}^{+4})$  and .67-order dependent upon intensity. *G* values for exchange (ions/100 ev) as large as 100 were obtained. The mechanism is apparently complex. The observed exchange results could be interpreted qualitatively in terms of an exchange chain (i)  $\text{Ti}^{+2} + * \text{Ti}^{+4} = \text{Ti}^{+3} + * \text{Ti}^{+3}$ , (rapid), (ii)  $* \text{Ti}^{+2} + \text{Ti}^{+3} = * \text{Ti}^{+3} + \text{Ti}^{+2}$  (rate determining), (iii)  $2 \text{Ti}^{+2} = \text{Ti}^{+3} + \text{Ti}^{+3}$  (chain terminating). Lefort & Lederer (112) observed a radiation-induced exchange between the 3 and 6 valence state of chromium in acid solution. The data indicate that in the radiation-induced reduction of chromate to chromous ion, OH radicals are removed according to the stoichiometry:  $\text{Cr}^{+6} + 3\text{OH} + \text{H}_2\text{O} = \text{HCrO}_4^- + 4\text{H}^+$ .

The radiolysis of aqueous hydrazine solutions with  $\gamma$ -rays and with

$\alpha$ -rays was studied by Lefort & Haissinsky (113). The mechanism proposed for the formation of ammonia, hydrogen, and nitrogen in oxygen-free systems is similar to that given in the earlier paper by Dewhurst & Burton (100), viz. (i)  $H + N_2H_4 = H_2 + N_2H_3$ , (ii)  $OH + N_2H_4 = N_2H_3 + H_2O$ , (iii)  $2N_2H_7 = (N_4H_6) = N_2 + 2NH_3$ . Nitrogen is the principal product of hydrazine oxidation in irradiated solutions containing oxygen. This oxidation proceeds through a chain reaction at pH values above 9.

Johnson (114) studied the chemical effects produced upon the dissolution in deaerated water of ferrous salts which had been irradiated in vacuo with 2 Mev cathode rays. Ferric ion, sulfite ion, and hydrogen were the observed products and had G values of 1.8, 0.43, and 0.35 respectively. The yields were independent of dose up to  $30 \times 10^{19}$  ev/gm. The fact that hydrogen production was the same regardless of whether there was ammonia or water of crystallization in the ferrous sulfate is interpreted as conclusive evidence that hydrogen arises from the action of the irradiated salt (trapped electrons) with water. Pucheault (115) reported additional information on the radiation chemistry of aqueous solutions of the o-phenanthroline and dipyriddy complexes of iron. Differences in the effect of pH on radiation yields in the two systems is interpreted in terms of the rates of dissociation of the complexes.

The  $\gamma$ -ray radiolysis of dilute oxygen-free formic acid solution at concentrations below .05 M and at pH values below 3 is consistent with the steps (i)  $H + HCOOH = H_2 + COOH$ , (ii)  $OH + HCOOH = H_2O + COOH$ , (iii)  $2COOH = HCOOH + CO_2$ , (iv)  $COOH + H_2O_2 = CO_2 + H_2O + OH$  [Hart (99)]. However, at higher concentrations, deviation from this mechanism is apparent in that (a) hydrogen yields are lower than predicted by the mechanism and (b) formaldehyde appears as a radiolysis product. It has been suggested [Hart (116)] that electron capture by formic acid,  $HCOOH + e = HCO + OH^-$  competes with electron capture by water  $H_2O + e = H + OH^-$  at the higher formic concentrations, and that HCO is removed via  $HCO + HCOOH = HCHO + COOH$ . Garrison, Bennett & Jayko (117) found that irradiation of dilute oxygen-free formic acid solutions with cyclotron-produced helium ions forms the reduction products glyoxal and glyoxylic acid in addition to formaldehyde. Smaller amounts of oxalic, glycolic, tartronic, mesoxalic, and tartaric acid are also observed. It is proposed that radiolysis of formic acid solutions under both the  $\gamma$ -ray and cyclotron conditions may be interpreted without the assumption of competing electron capture by solute if it is assumed that H adds reversibly to formic acid according to  $H + HCOOH \rightleftharpoons HC(OH)_2$ . At the high radical concentrations obtained in cyclotron irradiations  $HC(OH)_2$  combines with COOH to give glyoxylic acid or dimerizes to form glyoxal. In  $\gamma$ -ray irradiations the radical concentrations are lower, and H would be preferentially removed by the competing reaction  $H + HCOOH = H_2 + COOH$ .

Chemical reactions induced in aqueous glycine by radiation decomposition of water yield hydrogen, ammonia, acetic acid, and glyoxylic acids as principal products in oxygen-free systems [Maxwell, Peterson & Sharpless (118)]. The mechanism has been interpreted by Garrison & Weeks (119) in

terms of a reaction sequence initiated by (i)  $\text{OH} + \text{G} = \text{H}_2\text{O} + \text{G}'$ , (ii)  $\text{H} + \text{G} = \text{H}_2 + \text{G}'$ , (iia)  $\text{H} + \text{G} = \text{NH}_3 + \text{A}'$  ( $\text{G}' = \text{NH}_2\text{CHCOOH}$ ,  $\text{A}' = \text{CH}_2\text{COOH}$ ). Subsequent reaction includes (iii)  $\text{A}' + \text{G} = \text{A} + \text{G}'$ , (iv)  $2\text{G}' = \text{I} + \text{G}$ , (v)  $\text{G}' + \text{H}_2\text{O}_2 = \text{OH} + \text{H}_2\text{O} + \text{I}$  ( $\text{I} = \text{NHCHCOOH}$ ,  $\text{A} = \text{CH}_2\text{COOH}$ ). Hydrolysis of I, imino acetic acid, yields ammonia and glyoxylic acid. Supporting evidence for the formation of the proposed intermediates  $\text{CH}_2\text{COOH}$  and  $\text{NH}_2\text{CHCOOH}$  is found in the observation by Weeks (119) that succinic acid and its amino substituted derivatives are formed under conditions of high radical concentration obtained in cyclotron irradiations. At lower radical concentrations, e.g., in  $\gamma$ -ray irradiations it is assumed that  $\text{CH}_2\text{COOH}$  is preferentially removed via (iii). Radiation yields obtained (118) in x-ray radiolysis of oxygen-free 1 M glycine are in essential agreement with those calculated on the basis of the above mechanism in terms of accepted yield values for water decomposition.

The radiation chemistry of organic compounds in aqueous solutions containing ferric and cupric ions has been treated by Baxendale & Smithies (120). Product formation in oxygen-free systems can be represented by the reactions (i)  $\text{H} + \text{RH} = \text{R} + \text{H}_2$ , (ii)  $\text{H} + \text{Fe}^{+3}(\text{Cu}^{+2}) = \text{Fe}^{+2}(\text{Cu}^{+}) + \text{H}^+$ , (iii)  $\text{OH} + \text{RH} = \text{R} + \text{H}_2\text{O}$ , (iv)  $\text{Fe}^{+2} + \text{H}_2\text{O}_2 = \text{Fe}^{+3} + \text{OH} + \text{OH}^-$ , (v)  $\text{R} + \text{Fe}^{+3} + \text{H}_2\text{O} = \text{ROH} + \text{Fe}^{+2} + \text{H}^+$ , (vi)  $\text{Cu}^{+} + \text{Fe}^{+3} = \text{Cu}^{+2} + \text{Fe}^{+2}$ . The stoichiometry is given by  $\text{G}(\text{Fe}^{+2}) = \text{G}_p(\text{H}) + \text{G}_p(\text{OH})$ ,  $\text{G}(\text{ROH}) = \text{G}_p(\text{H}) + \text{G}_p(\text{OH}) + \text{G}_p(\text{H}_2\text{O}_2)$  and  $\text{G}(\text{H}_2) = \text{G}_p(\text{H}_2) + \text{G}_p(\text{H})$ . At low  $(\text{RH})/(\text{Fe}^{+3})$  or  $(\text{RH})/[(\text{Fe}^{+3}) + (\text{Cu}^{+2})]$  ratios, H reacts preferentially with  $\text{Cu}^{+2}$  or  $\text{Fe}^{+3}$  and under these conditions the values  $\text{G}(\text{ROH})$  and  $\text{G}(\text{H}_2)$  approach  $\text{G}_p(\text{OH}) + \text{G}_p(\text{H}_2\text{O}_2)$  and  $\text{G}_p(\text{H}_2)$  respectively. Product yields for a number of organic solutes were obtained and from these were calculated relative rates for the reactions (i)  $\text{RH} + \text{H}$  and (ia)  $\text{HCOOH} + \text{H}$ . Representative values for  $k_i/k_{ia}$  are: formic acid, 1.0; acetic acid, 0.10; acetone, 0.34; ethyl acetate 0.56; methanol, 1.5; formaldehyde, 4.7; deuterio formic acid, 6.8; ethanol, 14; sucrose, 35; benzoquinone,  $3 \times 10^3$ . It was also found that benzo- and duro-quinones can replace  $\text{Cu}^{+2}$  and  $\text{Fe}^{+3}$  in their reactions with organic radicals and hydrogen atoms.

In the interpretation of indirect action of radiation on organic solutes in oxygenated solutions it is generally assumed that H and OH are removed by the reactions (i)  $\text{H} + \text{O}_2 = \text{HO}_2$ , (ii)  $\text{OH} + \text{H}_2\text{M} = \text{HM} + \text{H}_2\text{O}$  (where  $\text{H}_2\text{M}$  represents the solute molecule). Observed yield data for a number of organic solutes are consistent with the conclusion (a) that  $\text{HO}_2$  does not react with the organic solute (b) that the subsequent reactions involve, (iii)  $\text{HM} + \text{O}_2 = \text{M} + \text{HO}_2$ , (iv)  $2\text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$  to give the yield relationships  $-\text{G}(\text{H}_2\text{M}) = \text{G}_p(\text{OH})$ ,  $\text{G}(\text{H}_2\text{O}_2) = \text{G}_p(\text{H}_2\text{O}_2) + \frac{1}{2}\text{G}_p(\text{OH}) + \frac{1}{2}\text{G}_p(\text{H})$ . For example, the oxidation of formic acid to carbon dioxide (99), the oxidation of lactic acid to pyruvic acid (121), and the oxidation of glycine to ammonia and glyoxylic acid (122) represent reactions which may be interpreted on this basis (i.e., termination through  $2\text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$ ). Putney & Pratt (123) have found that the x-ray-induced oxidation of the aqueous malic acid-oxygen system which gives oxalacetic acid as a major product can also

be interpreted in terms of reactions (i to iv) above. An initial value of 2.6 was obtained for  $-G(\text{malic})$  on the basis of the dosimetry value  $G(\text{Fe}^{+3}) = 15.6$ . A parallel oxidation path apparently yields  $\alpha$ -hydroxy- $\beta$ -keto succinic acid with the overall stoichiometry  $\text{H}_2\text{M} + \text{O}_2 = \text{MO} + \text{H}_2\text{O}$ . It would seem that this product could be formed through an organic-peroxy radical intermediate rather than through reaction of a malic acid radical with  $\text{HO}_2$  as proposed. The  $\text{Co}^{60}$   $\gamma$ -ray-induced oxidation of ascorbic acid in oxygenated 0.8 *N* sulfuric acid has been studied by Barr & King (124) and interpreted in terms of the yield of ferrous ion oxidation under similar conditions. It was found that  $-G(\text{H}_2\text{M})/G(\text{Fe}^{+3}) \simeq 0.5$  and  $-G(\text{O}_2)_{\text{H}_2\text{M}} / -G(\text{O}_2)_{\text{Fe}} + 2 \simeq 2.0$ . To obtain this stoichiometry it is necessary to assume (a) that both  $\text{HO}_2$  and  $\text{OH}$  react with ascorbic acid:  $\text{OH} + \text{H}_2\text{M} = \text{HM} + \text{H}_2\text{O}$ ,  $\text{H}_2\text{M} + \text{HO}_2 = \text{HM} + \text{H}_2\text{O}_2$ , (b) that the one electron oxidation product  $\text{HM}$  reacts with oxygen to form a peroxy radical:  $\text{HM} + \text{O}_2 = \text{HMO}_2$  and (c) that  $\text{HMO}_2$  is removed through the termination  $\text{HMO}_2 + \text{HM} = \text{M} + \text{H}_2\text{O}_2$  (or  $2\text{HMO}_2 = 2\text{M} + \text{H}_2\text{O}_2 + \text{O}_2$ ). Garrison & Weeks (122) interpreted the formation of ammonia and glyoxylic acid, the principal decomposition products in the radiolysis of oxygenated glycine solutions, in terms of the two oxidation steps  $\text{H}_2\text{M} + \text{OH} = \text{HM} + \text{H}_2\text{O}$  and  $\text{HM} + \text{O}_2 = \text{M} + \text{HO}_2$  where  $\text{M}$  represents the intermediate product imino acetic acid which, on hydrolysis, gives ammonia and glyoxylic acid. Calculated and observed yields for hydrogen peroxide, ammonia, and glyoxylic acid in 1 *M* glycine solutions are in essential agreement with this mechanism, although yield values for the latter two products appear to be somewhat higher than can be accounted for on the basis of indirect action alone. It is suggested from a consideration of radiation yields in both oxygenated and oxygen-free systems that as the concentration is increased, energy absorption by glycine contributes to ammonia and glyoxylic production through reaction involving excited glycine molecules. Secondary amines appear to be decomposed by indirect action in oxygenated solutions through processes similar to those which occur in aqueous glycine solutions. Jayko & Garrison (125) found that diethylamine, for example, gives ethyl amine and acetaldehyde, presumably through hydrolysis of the *N*-alkylimine oxidation product. It is pointed out that a similar mechanism may be involved in the radiation-induced decomposition of the  $-\text{NH}-\text{CH}_2-$  linkage in polypeptides.

Daniels, Scholes & Weiss (126) investigated further the nature of the aldehyde compound which is formed, in addition to the major product phenol, in the x-ray radiolysis of aqueous benzene solutions containing oxygen. It was found (a) that mucondialdehyde is the most likely aldehyde product and (b) that it is derived from a primary product of irradiation. Since aldehyde could not be detected in the oxygen-free systems, it is suggested that fission of the benzene ring is due to the formation of an organic peroxy radical leading, in turn, to a hydroperoxide from which water can be eliminated to give the dialdehyde product. The reaction sequence is assumed to be initiated by addition of  $\text{OH}$  to the benzene double bond. The proposed intermediate  $\phi(\text{H})\text{OH}$  could also be involved in the formation of phenol e.g.  $\phi(\text{H})\text{OH} + \text{O}_2 = \phi\text{OH} + \text{HO}_2$  [cf. Sworski (127)]. Garrison *et al.*

(128) studied the radiation (40 Mev helium ion)-induced oxidation of acetic acid in oxygenated aqueous solutions. Glycolic, glyoxylic, and oxalic acids are major products and have initial G values which are essentially independent of dose. Oxidation apparently occurs through parallel reactions initiated by formation of the common precursor  $O_2CH_2COOH$  via (i)  $CH_3COOH + OH = CH_2COOH + H_2O$ , (ii)  $CH_2COOH + O_2 = O_2CH_2COOH$ . It is proposed that the simplest mechanism for formation of glyoxylic acid in accord with the experimental results involves the steps (iii)  $2O_2CH_2COOH = 2OCH_2COOH + O_2$ , (iv)  $OCH_2COOH + O_2 = CHOCOHOH + HO_2$ . Glycolic acid is assumed to arise from a reduction of the intermediate  $OCH_2COOH$ . The formation of oxalic acid is interpreted on the assumption that some of the  $O_2CH_2COOH$  radicals are oxidized to give the intermediate  $O_2CHCOOH$  which isomerizes to  $(COOH)_2$ .

Dale (129) has shown that the radiation-induced oxidation of thiourea in oxygenated aqueous solutions occurs through a chain reaction. Quantitative measurements of yield values for formation of elemental sulfur,  $G(S)$ , show an induction period during which the yield increases to a maximum value and then remains constant. Each dose rate has a particular maximum  $G(S)$  value. The value  $G(S) = 1.7 \times 10^4$  was obtained at a dose rate of 0.71 r/min. The presence of oxygen is necessary for the chain to occur. No after-effect of irradiation is observed. Dale & Russell (130) found that cysteine, cystine, and glutathione protect catalase from radiation-induced inactivation in aqueous solution. Changes in catalytic activity, electrophoretic and chromatographic behavior and ultraviolet spectrum of the enzyme were followed.

A number of other aquo-organic systems of biological interest have been studied. Scholes, Weiss & Wheeler (131) found that organic hydroperoxides are major products in the x-ray radiolysis of aqueous nucleic acid systems containing dissolved oxygen. Total peroxide in the irradiated solution was determined by measuring the iodine liberated on addition of potassium iodide; hydrogen peroxide was measured by the titanium sulfate method. In a typical irradiation of deoxyribonucleic acid solution (0.1 per cent, Singer acid, pH ~ 7) with x-ray (200 kv.) in the presence of oxygen (1 atm.) with a total dose of  $\approx 3 \times 10^4$  rep, the yield of total peroxides was  $G = 2.5$ , whereas for hydrogen peroxide,  $G = 1.5$ ; this gives for the organic hydroperoxide yield,  $G = 1.0$ . The presence of molecular oxygen is essential for hydroperoxide formation which presumably involves an intermediate  $RO_2$  radical. Irradiation of aqueous purine and pyrimidine ribonucleotides has been shown by Daniels, Scholes & Weiss (132) to result in the formation of intermediate labile phosphate esters which lead to a postirradiation release of inorganic phosphate. This release of phosphate is apparently not the result of a slow attack of hydrogen peroxide on some relatively stable product of irradiation but is related to the formation, through radical attack, of activating carbonyl groups in the sugar components [cf. Wilkinson & Williams (133)]. Shooter, Pain & Butler (134) found that an increased susceptibility of deoxyribonucleic acid to heat can be induced by x-ray irradiation of the aqueous solution.



The sedimentation and viscosity data are in accord with the view that degradation results from the formation of breaks in the polynucleotide chain.

The action of  $\gamma$ -radiation on dilute aqueous solution of amylose was investigated by Bourne, Stacey & Vaughan (135). The initial attack on the amylose molecule is random rather than endwise, and the mechanism is multi-chain rather than single-chain. The glucose, maltose, and lower molecular weight products which were identified apparently result from direct attack on the amylose molecule (with accompanying fragmentation) rather than from attack on products liberated through hydrolytic cleavage. The production of acid groups (pK 4.5–5.0) was demonstrated. The value  $G(\text{RCOOH})$  was found to be 1.5 and 1.4 in oxygenated and evacuated solutions respectively and was independent of dose (and extent of degradation of the amylose) over the range studied. Two independent reactions (acid formation and degradation) are apparently involved. Kertesz *et al.* (136) measured viscosity changes associated with the  $\gamma$ -ray-induced degradation of pectin in aqueous solution.

The x-ray irradiation of oxyhemoglobin in aqueous solution was found by Barron & Johnson (137) to induce chemical change in the protein moiety, the porphyrin ring, and the valence state of iron. In the absence of oxygen, the ferri compounds of hemoglobin, hemin, cyanide hemochromogen, and cytochrome-*c* were reduced to the ferro form. Mee & Stein (138) found that cytochrome in oxygen-free aqueous solution ( $10^{-8}$  M, pH 7) containing benzoate or succinate (0.1 M) on irradiation with x-rays is reduced by organic free radicals derived from the second solute to give a product which is apparently identical with that formed by enzymic reduction. In the presence of methanol, ethanol, or *n*-butanol, a product is formed which is not identical with that of enzymic reduction. The latter radiation product is also formed in hydrogen-saturated solutions.

#### DOSIMETRY

The Fricke (ferrous sulfate) radiation-dosimeter is the chemical dosimeter most generally employed in current radiation research. The mechanism now generally accepted is in accord with studies on the effect of OH and  $\text{HO}_2$  radicals generated in ferrous sulfate solutions by other means and with other radiation studies of aqueous solution. The value of  $G(\text{Fe}^{+3})$  is, within experimental error, essentially constant for  $\gamma$ -rays, x-rays, and electrons over the energy range of from several Mev down to a few tenths Mev. At lower energies  $G(\text{Fe}^{+3})$  decreases in accord with the observed energy dependence of the radical and molecular yields for water decomposition.

Schuler & Allen (139) using the power input method have made a precise redetermination of the absolute yield of ferrous sulfate oxidation with 2 Mev cathode rays from a Van de Graff generator. Corrections for backscattering, charge transfer, and energy absorption in the cell windows were critically re-examined. An improved method of determining the energy of the cathode ray beam was employed. The reported yield  $G(\text{Fe}^{+3}) = 15.45 \pm .11$  represents



the most accurate calibration of the Fricke dosimeter made to date for light-particle radiation.

Ferricyields in air-saturated 0.1 *M* sulfuric acid were measured by Haybittle, Saunders & Swallow (140) for x-rays and  $\gamma$ -rays of effective mean energy ( $\bar{E}$ ) from 21 kev to 7.6 Mev. Energy absorption was estimated from ionization chamber measurements for which *W* (electron-volts per ion pair in air) was taken to be 34.0. The following  $G(\text{Fe}^{+3})$  values were obtained: (a) 60 kvp x-rays ( $\bar{E}=21$  kev),  $13.1 \pm 0.5$ ; (b) 100 kvp x-rays ( $\bar{E}=33$  kev),  $14.7 \pm 0.5$ ; (c) 220 kvp x-rays ( $\bar{E}=56$  kev),  $15.0 \pm 0.5$ ; (d) for  $\text{Co}^{60}$   $\gamma$ -rays ( $\bar{E}=1.25$  Mev),  $15.5 \pm 0.5$ ; (e) 30 Mev x-rays ( $\bar{E}=7.6$  Mev),  $16.3 \pm 0.6$ .

Cottin & Lefort (141) investigated the ferrous sulfate dosimetry of soft x-rays in air-saturated 0.1 *N* sulfuric acid solutions and obtained  $G(\text{Fe}^{+3})$  values of  $13.4 \pm .6$  and  $14.15 \pm .6$  for 8 kev and 10 kev x-rays respectively. Yields were based on ionization chamber measurements ( $W=34$  ev/ion pair). Papers by Trumbore & Aten (142) and LeBail & Sutton (143), although not primarily dosimetry studies, involve closely related work on ferrous sulfate solutions. The former reports a study of the action of  $\text{Co}^{60}$   $\gamma$ -rays on air-saturated ferrous sulfate solutions in light and heavy water 0.8 *N* in sulfuric acid. Assuming  $G(\text{Fe}^{+3})=15.5$  for the standard dosimeter, *G* values of  $16.1 \pm .2$ ,  $17.0 \pm .5$  and  $18.6 \pm .8$  were found for  $\text{H}_2\text{O}=\text{D}_2\text{O}$  mixtures of 55, 85, and 98 atom per cent D respectively. The effect of  $\text{D}_2\text{O}$  on  $G(\text{Fe}^{+3})$  is interpreted in terms of the yield measurements for  $\text{D}_2\text{O}$  decomposition reported by Hart & McDonnell [7, p. 593]. In the study by LeBail & Sutton no effect of oxygen pressure (up to 14 atm.) on  $G(\text{Fe}^{+3})$  yields could be detected.

The energy required to produce an ion pair in air for  $\text{Co}^{60}$   $\gamma$ -rays was determined calorimetrically by Bernier *et al.* (144) using a 1000-curie cobalt source. An average value of  $W=33.0 \pm 0.3$  ev/ion pair was obtained. A review of some of the more recent work on the determination of  $W_{\text{air}}$  is given. Emery (145) also has discussed the use of the ionization chamber in the measurement of radiation absorption.

Problems associated with the use of accelerators in obtaining radiation chemical data of maximum realizable accuracy and precision have been treated by several authors. Schuler & Allen, in the paper referred to above (139), demonstrated for the condition of complete absorption that it is possible, by the power input method using Van de Graff cathode rays, to obtain an absolute accuracy of about 0.5 per cent (probable error) and a precision in relative measurements of about 0.2 per cent. Lemmon & Mosier (146) have developed dosimetry methods and equipment for the irradiation of thin, solid organic samples with electrons (at energies above 2 Mev) from an accelerator. The entire electron beam is allowed to pass through the sample and to impinge on an electron collector (Faraday cup) mounted behind the sample holder. The effect of secondary emission on the dosimetry is evaluated. Energy given to the sample is calculated from Feather's rule. With 5 Mev electrons it is estimated that the dosimetry is valid to within  $\pm 10$  per cent. Hart, Ramler & Rocklin (103) reviewed the requirements for accurate

cyclotron-beam monitoring under irradiation conditions in which the beam is allowed to pass through a glass or other nonconducting window which insulates the target from ground. It is shown that collection of current in this manner introduces error in that the beam causes a net displacement of electrons across the insulating window. The error can be evaluated separately by measuring the displacement current [see also Schuler & Allen (147)], or it can be eliminated by connecting the cyclotron window (electrically isolated from the cyclotron) to the target cell so that the entire target assembly acts as a Faraday cage [see also Garrison *et al.* (148)].

Other related work includes: the evaluation by Pucheault (149) of several chemical and physical methods for mixed-radiation dosimetry in a nuclear reactor; studies on glass dosimetry by Riegert, Johns & Spinks (150), Davidson, Goldblith, & Proctor (151), and Kreidl & Blair (152); the development of the nitrous oxide system for high-level dosimetry by Harteck & Dondes (30); the study by Hilsenrod (153) of the effect of added organic solutes on the response of the chloral hydrate dosimeter.

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# QUANTUM THEORY<sup>1</sup>

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This article is divided into two main parts, one dealing with transfers of energy between vibrational and translational degrees of freedom, and the other with valency and the electronic structure of molecules.

## VIBRATIONAL ENERGY TRANSFER IN GASES

A better understanding of the factors influencing the ease of transfer of energy from vibrational degrees of freedom to translational has emerged in the last few years, due both to the steady accumulation of experimental data and to the appearance of an improved quantum mechanical method of calculating approximate deactivation probabilities [Slawsky, Schwartz & Herzfeld (1); Takayanagi (1a)].

As has long been known, vibrational to translational energy transfer is an inefficient process. Consequently, during a rapid compression of a gas, as for example in a high frequency sound field, vibrational degrees of freedom (and in some cases rotational degrees) are unable to adjust themselves immediately to the temperature of the translational degrees. There is a lack of equipartition of energy between internal (vibrational) and external (translational) degrees, which can be represented in a formal manner by a relaxation equation (2, 3),

$$\frac{\partial T'}{\partial t} = -\frac{1}{\tau} (T' - T(tr.))$$

where,  $T'$ , is the instantaneous temperature of a particular degree of freedom and  $T(tr.)$  is the temperature of the external degrees.  $\tau$  is the relaxation time.

Usually, the transfer between rotation and translation is an efficient process (4 to 9), and in the ensuing discussion rotation will be considered as if it were a translational degree of freedom.

Several experimental methods have been used for the measurement of  $\tau$ . They have been reviewed elsewhere (10, 11), and here it will suffice to enumerate the more important. These are: (a) the measurement of the dispersion and absorption of supersonic waves, (b) the measurement of the entropy increase brought about by the rapid stoppage of a jet at an impact tube (12), (c) the consideration of the density changes in the zone immediately behind a shock wave (9, 13, 14). A recent direct method involving infrared irradiation has been discussed (15, 16, 17).

Quantum and classical mechanics set out to calculate not  $\tau$  (at least not directly) but the probability,  $P$ , of a vibrating molecule being deactivated, on collision, with another atom or molecule. The symbol,  $P_{i \rightarrow f}$ , denotes the probability of the simple deactivation of a particular mode from initial state,

<sup>1</sup> The survey of literature pertaining to this review was concluded in November, 1956.

$i$ , to final state,  $f$ . Complex deactivation, of probability,  $P_{i-f}e^{-h}$ , can also be distinguished (1), in which, on collision, mode  $a$  changes its state from  $i$  to  $f$  and simultaneously mode  $b$  changes its state from  $g$  to  $h$ , only the difference in energy,  $h\nu_a - h\nu_b$ , being transferred to translation. Deactivation by radiation is always ignored (18).

Before experimental and theoretical results can be compared, an equation must be found relating  $P$  and  $\tau$ . For the simplest possible case, in which there is only one vibrational degree of freedom and transitions are only possible between the ground and first excited states, then (11):

$$\tau = [Z \cdot P_{1-0}(1 + e^{-h\nu/kT})]^{-1}$$

where  $Z$  is the number of collisions a molecule experiences per sec. and  $h\nu$  is the value of the vibrational quantum transferred. For many cases  $\exp. (-h\nu/kT) \ll 1$  and  $\tau \approx (Z \cdot P_{1-0})^{-1}$ . That is,  $\tau$  approximately equals the mean life time of a molecule in the excited state.

For gases composed of polyatomic molecules, or a mixture of different diatomic molecules, both simple and complex excitations are possible and separate relaxation times govern each type of exchange. Equations relating such relaxation times, which in principle can be determined from experiment, to the probabilities  $P_{1-0}$ ,  $P_{1-0}e^{-1}$ , etc. are rather complex and will not be discussed here (see 1, 18 for recent discussions). For most polyatomic gases which have been investigated, only one measurable relaxation time is found [Lambert *et al.* (19, 20, 21); Rossing & Legvold (22)]. This is in accord with the idea (19), that vibrational energy is usually taken up from translation only by the lowest mode, with a characteristic relaxation time  $\tau_1$ , and is then transferred to other vibrational modes, on collision, much more rapidly. A simple relationship then exists between  $\tau_1$  and  $\tau$ , the effective relaxation time which governs the whole process [see Rowlinson & Lambert (19)]. Busala *et al.* (23) have found two distinct relaxation times for  $\text{CH}_2\text{Cl}_2$ . Cheng (24) has also found that the dispersion of sound in benzene can be accounted for, either by one or two relaxation times.

*Calculations of probability,  $P$ .*—All theoretical methods of calculating probabilities of deactivation contain simplifying approximations, the validity of which can only be judged by comparison with experiment. Agreement to better than order of magnitude cannot be expected. Two main approaches have been used: (a) the semiclassical, and (b) the wholly quantum mechanical.

*Semiclassical.*—Here classical dynamics are used to discuss encounters, and the results of quantum mechanical time-dependent perturbation theory to discuss the actual transition. Such an approach requires the evaluation of the "perturbation integral." A discussion of this topic has been given recently by Cottrell & Ream (25).

By a purely classical and qualitative argument, Landau & Teller (26) concluded that for the collision of an atom  $A$  with a diatomic molecule  $BC$ , the efficiency of energy transfer between vibration and translation would be



small if the discriminating ratio, time of collision/period of vibration  $\gg 1$ . More specifically they assumed the probability of transfer,  $P_{(\omega)} \propto \exp[-4\pi^2\nu a/\omega]$  where  $\nu$  is vibration frequency of BC,  $\omega$  the relative velocity of approach, and  $2\pi a$  a length of the order of gas kinetic radii, is characteristic of the intermolecular forces. This assumption follows (25, 26) from a time-dependent perturbation calculation which assumes an exponential repulsion between B (or C) and A, and zero impact parameter (i.e., head-on collision). For normal (gas kinetic) velocities, and typical vibration frequencies, the discriminating quantity  $4\pi^2\nu a/\omega \gg 1$ , and consequently the probability of transfer is very small.

To obtain an average probability,  $P$ ,  $P_{(\omega)}$  must be integrated over a Maxwellian distribution of velocities for all values of  $\omega$  from 0 to  $\infty$ . In fact, only a small range of velocities, about  $\omega_{\max}$ , contribute appreciably to the integral, and so the latter can be evaluated by an approximate method [see Jeffreys & Jeffreys (27)]. Landau & Teller obtained as a final result:

$$P \propto \exp \left[ - \left( \frac{54\pi^4 a^2 \nu^2 M}{kT} \right)^{1/3} \right] \quad (I)$$

These authors distinguished between adiabatic and nonadiabatic processes. An adiabatic force, in this context, means one that changes infinitesimally during a period of vibration. They concluded that only nonadiabatic forces can induce transitions, and consequently transition probabilities are determined principally by short-range repulsive forces.

*Quantum mechanical.*—The development of a quantum mechanical approach is attributable to several authors, chiefly Zener (28), Jackson & Mott (29), and Slawsky *et al.* (1). Following (1), the method can be outlined in the following way.

At the simplest level, the collision between two diatomic molecules, assumed to be rotationless, is supposed to take place in one dimension along the line of centres. For mathematical reasons, it is expedient to express the interaction potential of the two nearest atoms (the others are neglected) in an exponential form  $V = V_0' \exp(-\alpha X)$ .  $X$  is the distance between the two nearest atoms and  $V_0'$  and  $\alpha$  are constants. If  $s_1$  and  $s_2$  are the normal coordinates for the vibrations of AB and CD respectively, and  $r$  is the distance between their centres of gravity, then,  $X = r + A_0 + A_1 s_1 + A_2 s_2$ . Here  $A_0$  is a constant dependent on the equilibrium bond lengths of AB and CD, and on the atomic masses;  $A_1$  and  $A_2$  are constants dependent only on the atomic masses. Then  $V = V_0 e^{-\alpha r} \cdot e^{-\alpha A_1 s_1} \cdot e^{-\alpha A_2 s_2} = V_0 V_r(r) V_1(s_1) V_2(s_2)$ . The values of  $\alpha$  and  $V_0$  are determined by fitting the "s" independent part of  $V$  to the Lennard-Jones potential,  $V = 4\epsilon[(r_0/r)^{12} - (r_0/r)^6]$ , in such a way that the magnitudes,  $V$ , and slopes  $\partial V/\partial r$  are equated at the classical distance of closest approach;  $\alpha$  is derived as a function of  $r_0$ ,  $\epsilon$ , and  $v_0$ , the relative velocity of approach.

The relative motion of the two molecules, before and after impact, is represented by waves, distorted by the average interaction between the two

systems in the initial and final states respectively. [Method of distorted waves (30)].

If the colliding molecules were originally of relative velocity,  $v_0$ , and vibrational states  $i_1, i_2$ , then the probability,  $P(v_0)^{i-f}$ , that on collision the molecules will change their vibrational states to  $f_1, f_2$ , and their relative velocity to  $v_f$ , is given by,

$$P(v_0)^{i-f} = \frac{64\pi^2 V_0^2}{v_0 v_f h^3} \left[ V_{(i_1-f_1)} \cdot V_{(i_2-f_2)} \int_{-\infty}^{+\infty} F_0 F_F V_r \cdot dr \right]^2$$

where  $F_0$  and  $F_F$  are the wave functions for a free particle in the field  $V_0 e^{-\alpha r}$ . The matrix elements,  $V_{(i_n-f_n)}$ , are defined by:  $V_{(i_n-f_n)} = \int_{-\infty}^{+\infty} \psi_i^{(n)} V_n^{(n)} \psi_f^{(n)} ds_n$ , where  $\psi_i$  and  $\psi_f$  are normalised simple-harmonic oscillator wave functions for the  $s_n^{\text{th}}$  normal coordinate.  $V_{1-0} = -\alpha A [h/8\pi^2 \mu \nu]^{1/2}$ , where  $\nu$  is the vibration frequency and  $\mu$  the reduced mass of the oscillator;  $V_{0-0} = 1$ .

The integral  $\int_{-\infty}^{+\infty} F_0 F_F V_r \cdot dr$  can be evaluated for an exponential field [Jackson & Mott (29)], and that is why this particular form of  $V$  is used here. The expression for  $P(v_0)^{i-f}$  is averaged over a Maxwellian distribution of velocities and the resulting integral again approximated to, in the same way as for the semiclassical result. The resulting expression for  $P^{i-f}$  is,

$$P^{i-f} = V_{(i_1-f_1)}^2 V_{(i_2-f_2)}^2 \times 1.56 \left[ \frac{8\pi^2 M \Delta E}{(\alpha^*)^2 h^2} \right]^2 \sigma^{2/3} e^{-\sigma}$$

where,

$$\sigma = 3 \left[ \frac{2\pi^4 (\Delta E)^2 M}{(\alpha^*)^2 h^2 k T} \right]^{1/3} \pm \frac{\Delta E}{2kT}$$

$\Delta E$ , equal to  $M/2(v_0^2 - v_f^2)$ , is the total energy exchanged between vibration and translation during the collision (plus for activation, minus for deactivation).  $\alpha^*$  is the value of  $\alpha$  for the most effective velocity, i.e., for the value of  $v_0$  which makes the integrated form of  $P^{i-f}$  a maximum. This expression is only valid when  $\Delta E$  represents a large fractional change in momentum and  $\exp(-4\pi^2 \Delta E / \alpha^* h v_0^*) \ll 1$ . Approximately,

$$P^{i-f} \propto \exp \left[ - \frac{54\pi^4 M}{(\alpha^*)^2 h^2 k T} \right]^{1/3} \quad (\text{II})$$

which is just the dependence of  $P$ , on  $\nu$ ,  $M$ , and  $T$ , predicted by the classical expression (I). In fact, it can be shown [Zener (31)] that the wholly quantum expression reduces to the semiclassical value if  $v_0 \sim v_f$ , i.e., if the motion of the incident atom is not sensibly affected by the energy exchange. The details of this calculation have been somewhat refined in more recent papers [Schwartz & Herzfeld (32); Tanczos (18)]. In (32), the problem is treated as a three dimensional collision process, and a factor  $e^{4/kT}$  introduced to allow for the velocity gains of molecules when moving through the attractive well of the Lennard-Jones potential. In (18) the treatment of some polyatomic molecules by this method is dealt with. The refinements of (32) do not affect

the  $P$  values by a factor of more than ten and in no way destroy the dependence of  $P$  on  $M$ ,  $\nu$ , and  $T$ , as given by (II).

*Comparison of experiment and theory.*—Calculated values of  $Z_{1-0}$  ( $= (P_{1-0})^{-1}$ ), for several simple diatomic and triatomic molecules, are compared with experimental values in Table I (33).

TABLE I  
COMPARISON OF CALCULATED AND EXPERIMENTAL  $Z_{1-0}$  VALUES

Gas Partners	$\alpha^{-1}(\text{\AA})$	$M$	$\Theta = \frac{h\nu}{k} \text{ } ^\circ\text{K}$	$T^\circ\text{K}$	$Z_{1-0}$ calc.	$Z_{1-0}$ exptl.
$\text{N}_2\text{--N}_2$	0.211	14	3380	600	$1.5 \times 10^9$	$2 \times 10^7$
$\text{O}_2\text{--O}_2$	0.189	16	2260	288	$1.0 \times 10^8$	$2.5 \times 10^7$
$\text{O}_2\text{--H}_2$	0.173	1.88	2260	288	1,100	20,000
$\text{Cl}_2\text{--Cl}_2$	0.189	35	810	288	13,000	34,000
$\text{Cl}_2\text{--He}$	0.180	3.78	810	288	75	900
$\text{Cl}_2\text{--N}_2$	0.195	20	810	288	9,500	43,000
$\text{CO}_2\text{--CO}_2$	—	44	959	288	22,000	50,000

The form of (II) leads to the conclusion that the exchange of vibrational energy, at a given temperature, shall occur more readily for (a) small effective mass  $M$ , and (b) small  $\Delta E$ . Both conclusions are fairly well supported by these data, for pure gases and for mixtures. The absolute values of  $Z_{1-0}$  agree to order of magnitude; for these particular gases there is no likelihood of chemical interaction. Slawsky *et al.* (1) suggest reasons for the large effect that impurities can have on the ease of transfer. Thus, the probability of transfer can be increased enormously if the foreign molecule has either a much smaller mass than that of the pure gas molecule, or possesses energy levels close to those of the other molecules. In the latter case, a complex deactivation is possible, in which a pure gas molecule loses a quantum ( $h\nu_1$ ), in collision with a foreign molecule, and simultaneously the latter takes up a quantum ( $h\nu_2$ ) only the small difference in energy,  $\Delta E = h\nu_1 - h\nu_2$ , goes to translation. The quantum mechanical approach is not suitable for dealing with strongly attractive "chemical" forces, since the wave equation for a free particle in such a field cannot be solved analytically. Widom & Bauer (34) have described a semiclassical treatment of this type of problem, using  $\text{CO}_2\text{--H}_2\text{O}$  as an example. The high probability of transfer is essentially due to the high velocity of approach, caused by the large attractive forces, making the discriminating ratio  $av/\omega$  small and hence  $P$  large.

A summary of experimental results for more complex molecules can be found in (19 to 23, 35, 36). The values of  $P_{1-0}$  are considerably higher than for simple molecules, since minimum vibration frequencies are usually much lower, and hence,  $\Delta E$  smaller. An apparent discrepancy between the experimental and theoretical dependence of  $P_{1-0}$  on  $M$  now appears. Lambert *et al.*

(20, 21) found the expression,  $P_{1-0} \propto \exp(-\text{const. } \nu_{\text{min}})$  described their results for certain organic halides. Rossing & Legvold (22) deduced a similar expression for 14 halogenated methanes, no dependence of  $P_{1-0}$  on mass being found. The results of Busala *et al.* (23) do not support those of Lambert *et al.* too well. The latter found that  $P_{1-0}$  could also be correlated with the infrared activity of  $\nu_{\text{min}}$ , the lowest vibration frequency in the molecule.  $P_{1-0}$  was found to be appreciably higher when  $\nu_{\text{min}}$  was infrared active. This suggests that an oscillating dipole may superimpose a periodic term on the intermolecular force function, which can facilitate energy transfer. This possibility has been investigated theoretically by Slawsky & de Wette (37). They find the effect of dipole-dipole interaction to be twofold: (a) the oscillatory dipole-dipole interaction can perturb the vibrational energy levels of the oscillator, but even for a large molecular dipoles this effect is vanishingly small at collision distances; (b) the permanent dipole-dipole (or quadrupole-quadrupole) attraction increases the relative velocity of approach and can lead to a very slight increase in  $P_{1-0}$ . This is an example of the small effect that long-range (near adiabatic) forces have on transition probabilities. Experimental evidence (38) for this view is provided by the finding that *cis*- and *trans*-dichloroethylene have practically the same relaxation times, despite the fact that these isomers have different dipole moments.

A "mass effect," as predicted by theory, is found experimentally for the vibrational deactivation of a fairly complex molecule, ethylene, by simple molecules  $\text{N}_2$  and  $\text{H}_2$ ,  $\text{H}_2$  being more than 10 times as effective as  $\text{N}_2$  [McGrath & Ubbelohde (39)]. But at the moment there seems to be no ready explanation for the absence of a "mass effect" for collisions between complex molecules. A partial independence of mass, even for comparatively simple molecules, seems to be found for the relative efficiencies of inert gases in promoting certain unimolecular decompositions (40); but here it must be remembered that collisions of highly excited molecules are involved, and smaller quanta will be exchanged than for transitions between ground and first excited states, (which are the important ones in ultrasonic experiments). Moreover, the presence of more highly excited molecules may introduce new factors into the intermolecular force function.

Lambert *et al.* (20) and Legvold & Rossing (22) have suggested, that for complex molecules,  $P_{1-0}$  depends upon the average kinetic energy of approach rather than upon the velocity of approach, which is the supposition of both the classical and quantum theories. Vibrational energy transfer is then regarded as a process involving passage over an energy barrier, height,  $\epsilon$ , where  $\epsilon = nh\nu_{\text{min}}$ . The probability of such a process occurring in a single collision is given by  $P \propto \exp[-\epsilon/kT]$ ;  $P_{1-0}$  is then independent of mass and is of the correct empirical form,  $\exp[-\text{const. } \nu_{\text{min}}]$ . This theory creates certain difficulties. It is hard to justify theoretically and is unable to account for experimental findings for simple molecules; also it predicts a temperature coefficient many times too large (20).

An apparent independence of  $P_{1-0}$  on mass would be found if  $\alpha^*$  in (II)

were not constant, for a series of related molecules, as is sometimes assumed (22), but varied in such a way as to compensate, to some extent, changes resulting from differences in mass. Recent calculations by Tanczos (18) on methane and methyl chloride suggest this. For methane,  $\alpha^*$  was matched to the Lennard-Jones potential, but for the polar methyl chloride the more realistic Krieger potential (41) was used. The calculated relaxation times for these two molecules agree very well with experiment, but if the same  $\alpha^*$  values had been used for the two molecules, no agreement could have been reached. This draws attention to the largest failing of the theory at the moment, which is a lack of knowledge of the correct intermolecular potential (contained in  $\alpha^*$ ) to be used at the short distances important in energy transfer. Cottrell & Ream (25) have pointed out that the second virial coefficient gives almost no information about the nature of the forces at these small distances. They have suggested an appropriate intermolecular potential for methane derived from a consideration of interatomic forces. Some recent experimental work, which may be of use in assigning a correct intermolecular potential, is that of Amdur *et al.* (42) on the high energy scattering of neutral molecules.

This same lack of knowledge probably accounts for the failure of expression (II) to account for the variation of  $P_{1-0}$  with temperature. Very few temperature coefficients have been measured over any appreciable range of temperatures. The result of Eucken *et al.* (43) for  $N_2O$ ,  $CO_2$  and  $CH_4$ , all show  $\log_{10} P_{1-0} \propto -T^{-1/3}$ , but the slope predicted by (II) is too steep, i.e., to get agreement, a value of  $\alpha^*$  must be chosen which is unreasonably large, and which causes the calculated value of  $P_{1-0}$  to be in error by several powers of ten.

The transfer of rotational energy to translation has been treated, quite successfully, by a method analogous to the quantum mechanical approach outlined here for vibrational transfer [Brout (44)].

#### ELECTRONIC STRUCTURE OF MOLECULES\*

This report will be concerned mainly with ground states of molecules. The last few years have seen much more detailed treatments of the electronic structures of a greater number of simple molecules. These have been based to a large extent on the SCF procedure of Roothaan (45), and have been made possible by the availability of high speed computing machines. There have been several treatments of  $H_2O$  and  $NH_3$  and molecules of like complexity, though these have usually been less detailed than those of diatomic molecules. In addition there are the calculations for more complex molecules in which only some of the electrons (e.g.,  $\pi$ ) are treated. In the last case, the form of the potential field is an approximate one attempting to take account of the nuclei and of the electrons in the other orbitals (46). It is difficult to know

\* The following abbreviations will be used: AO, atomic orbital; MO, molecular orbital; LC, linear combination of; CI, configuration interaction; SCF, self consistent field.

how reliable this is. Also the wave functions, usually in terms of MOs, are inevitably approximate for the restriction is always imposed that they are of the LCAO type, the AOs themselves being approximate. In more complex treatments the limitation of these approximations is reduced by allowing resonance with excited states (so-called CI) so that a better wave function is obtained as a combination of separate wave functions. Therefore, with the  $\pi$  electron treatments both the potential field and the orbitals must be approximate and this double uncertainty causes the results to be unreliable, though it is difficult to see how else complicated systems are to be tackled at the moment. The much more complete recent treatments of diatomic molecules usually involve a consideration of all the electrons separately (sometimes the 1s are excluded) so that the potential field is exact, though this has, so far, restricted consideration to molecules containing rather few electrons. However, the LCAO approximation, which is almost always used, still places a limitation on the form of the wave function. The next stage may lie in the removal of this limitation, and perhaps some form better than the LCAO for the orbitals in the region between the atoms may be proposed. There is also the ever present problem of how to include terms involving electron separation in the wave function preferably in some explicit form (47). Could progress be made with this, considerable improvements would result but there are few signs of such a development.

A recent change that affects greatly molecular structure theory is that data of quite new types are becoming available for molecules, radicals and ions, and this must help theoretical chemists in developing more satisfactory wave functions. In the pre-war decade, the data available were primarily bond lengths and angles, dipole moments, dissociation energies, and some magnetic data. There continues to be great stress laid on computing values for dissociation energies as a test of any treatment. This may be a mistaken policy for as Mulliken has said, "the reliable computation of dissociation energies will probably remain for some time a hard nut to crack" (48). This arises because the energy separation between two systems of very different type is involved, and this separation is a small percentage of the total energy. From 1930 to 1940 one of the most direct pieces of information about the electronic structure was the dipole moment. Now there is a steadily increasing and varied knowledge of the electron cloud. For example, quadrupole coupling coefficients from microwave spectra allow the determination of the electric field gradient at the nucleus due to the electrons around it. There are also nuclear and paramagnetic resonance spectroscopic measurements which give information about electron distributions. In addition, ionisation potentials can now be obtained with increasing accuracy and in greater variety (49), and molecular quadrupole moments are sometimes available. The intensities of infrared bands give information about the changes occurring in the dipole moment on distorting the molecule. It seems surprising that this has not been used much more by theoretical chemists particularly as unexpected effects are observed. The intensities of Raman lines may also prove useful

but there has been less progress here. With greater knowledge of Coriolis coefficients, isotope effects, and centrifugal stretching, much more reliable knowledge is available of molecular force fields so that, instead of comparing molecular and atomic energies, changes in energy for configurations near the equilibrium one can be used with perhaps greater advantage. However, the major recent improvement is probably the increased information of a more or less direct kind that is available about the electron distribution.

*Some simple systems.*—During the last two years there has continued to be an interest in very simple systems [e.g., He (50),  $H_2^+$  (51),  $H_2$  (52 to 55),  $HeH^{++}$  (56),  $HeH^+$  (57),  $HeH$  (58),  $H_3^+$  (59, 60, 61),  $H_3$  (62),  $H_3^-$  (63)]. The object of dealing with these is sometimes a specific one (e.g.,  $HeH^+$  in relation to the  $\beta$  decay of HT) but more usually it is to examine a system so simple that there is hope of reaching a sufficiently correct result without too great an expenditure of time. By so doing, a general understanding may be obtained which is useful in providing guiding principles for more complex situations. With this object Eyring *et al.* (63) have studied  $H_3^-$  selected because it has more electrons than  $H_3^+$  and  $H_3$  (which have also been treated for similar reasons) and so exemplifies better effects to be found in more complex systems. They test the Sklar and Ruedenberg-Mulliken type integral approximations and compare the results with those obtained both for Heitler-London and Wang treatments, using actual integral values. They conclude that the Mulliken type approximation is to be preferred.

For  $HeH^{++}$  containing only one electron, exact wave functions have been obtained for five states (56). Four ( $1s\sigma$ ,  $2s\sigma$ ,  $2p\pi$ , and  $3d\sigma$ ) are repulsive, while  $2p\sigma$  has an equilibrium bond length of 2.06 Å and a small dissociation energy of 0.85 eV.  $HeH^+$  has been examined by Evett (57) using a Coolidge-James type of treatment, as did Toh (64), but he employed 20 and 23 terms in his series instead of 10. He found a dissociation energy of 1.90 eV, dissociation being to He and  $H^+$ , and a vibration frequency of  $3600\text{ cm}^{-1}$ .

There has been a continuing interest in  $H_2$ . Callen (53), whose paper contains a useful table summarizing various treatments of  $H_2$ , has tested three functions. In the first, an MO in elliptic coordinates was used, the wave function being a simple product of two similar one electron functions; the binding energy was only 3.54 eV. For the second and third functions, Callen added to the above simple function one and two others respectively, the treatment being therefore of the CI pattern. With his three configuration function he obtained a binding energy of 4.276 eV, the best calculated value except for that of Coolidge and James. He concluded that the combination of functions that proves useful is one which introduces effectively in-out electron correlation (65). Wallis (54) has also designed a function to take account of correlation. It is of the form  $\psi_A(1)\cdot\psi_B(2)+\psi_A(2)\cdot\psi_B(1)$ , the electrons being numbered and  $\psi_A$  and  $\psi_B$  being simple LCAO MOs but involving different effective charges ( $Z_A$  and  $Z_B$ ). The energy is minimized at a dissociation energy of 3.565 eV with  $Z_A=1.5$  and  $Z_B=0.9$  showing that the function incorporates in-out correlation. Using a function with a variable ratio of homopolar to



ionic terms but still having two effective nuclear charges (now 1.4 and 1.0) the energy was minimized at  $D=4.08$  ev. The energies calculated are only fair but the merit of the treatment is that electron correlation appears clearly. Shull & Hagstrom (55), following a suggestion of Shull & Löwdin (66), have applied a wave function centred on the mid-point of the bond to the treatment of  $H_2$  only  $s$ -type orbitals being used. The binding energy obtained is only slightly less good than Heitler-London-Sugiura's, which is interesting since the spherical orbitals appear to be inappropriate. The approximate natural orbitals (67) have been derived and it is concluded that correlation effects are less important than in the helium atom (53, 54).

The molecule  $Li_2$  has been studied in detail and Kotani has given some of the results (68). The conclusion is that the Heitler-London is much better than the MO method in their first approximations. Another important feature seems to be that great improvement is obtained if the  $2s$  orbital is modified by combination (hybridisation) with a  $2p$  orbital (i.e., polarised by the procedure of Rosen) leading to an additional electron concentration between the nuclei. Including  $\pi$  structures is also advantageous presumably because of electron correlation effects.

Another six electron system that has been treated in detail is BH, at the observed bond length by Sahni (69) and over a range by Boys *et al.* (62). [ $LiH$  and  $BeH^+$  were treated by Fischer-Hjalmars (70)]. An SCF LCAO MO treatment was used by Sahni, all electron interactions being included specifically. A second treatment was also used in which inner shell ( $1s$ )-outer shell mixing was neglected (but all orbitals were made orthogonal to one another). The total energy of boron and hydrogen atoms infinitely separated was calculated to be  $-680.0$  ev. The complete calculation for BH gave an energy of  $-681.8$  ev, and the less complete one  $-681.7$  ev (obs. dissociation energy is  $2.6$  ev). Even in this relatively simple case, the binding energy is a small proportion of the total energy so that a small error in this can lead to a large percentage error in the dissociation energy. Sahni's figures show that the difference between the calculated and observed total energy ( $5.2$  ev) is greater than the observed dissociation energy. The neglect of inner-outer shell mixing is not serious as regards the total energy but may be as regards the dissociation energy. The dipole moment was calculated to be  $0.99$  D and an electron distribution analysis [atomic and overlap populations (48)] was given. Boys & Cook (62) have just presented some results for BH obtained using a high speed automatic computing machine. Because the maximum use is made of the machine an extremely flexible form can be used for the wave function, the variational method being used. Calculations have been carried out for three BH distances and the bond length is obtained in exact agreement with experiment. The force constant is about 50 per cent greater than the experimental value and the binding energy is calculated to be about  $1.5$  ev, the total energy being a little greater than that obtained by Sahni. The great merit of this method of Boys *et al.* is that the procedure can be applied with unlimited accuracy.

The nitrogen molecule has been treated similarly by Scherr (71), all 14 electrons being included. The calculated total energy is good, being 0.9905 of the observed, but the calculated dissociation energy of 1.2 eV agrees poorly with the observed (9.9 eV). This is not surprising since the calculated dissociation energy is only 0.04 per cent of the total energy which is itself in error by 1 per cent. A treatment using MOs involving no inner-outer shell mixing gave a much better value for the dissociation energy. The complete treatment gave a quadrupole moment of  $-1.87$  au. (experimental 1.11). Scherr lists the errors in calculated total energies for a number of molecules for which complete (in the above sense) or nearly complete treatments have been made. These range from 0.6 to 1.1 per cent.

Kopineck treated  $N_2$  as a 10 electron problem (72) and Brüchner (73) has treated it as a 6 electron problem, the available six  $2p$  electrons being used for the three covalent bonds. The calculated dissociation energy was 9.98 eV and the bond length 1.115 Å (obs. 1.0976). An electrostatic force calculation (74) was also carried out as a 14 electron problem (73) leading to a dissociation energy of 9.89 eV. There are no details of these calculations. Their success, as compared with the more complete treatments, may be fortuitous but it is also possible that the complete treatments are less good than the partial ones for calculating dissociation energies because of the very large energies of inner shell electrons, slight changes in which make a great difference to the calculated dissociation energy.

Sahni (75) treated CO in a manner comparable, though less complete, to that of Scherr for  $N_2$ . The total energy was within 1 per cent of the true value. The author presents interesting contour diagrams of the various orbitals showing, for example, that the  $\pi$  orbitals are a maximum in the plane through the oxygen atom perpendicular to the molecular axis. Calculated ionisation potentials are given; these agree well with the observed ones. The calculated dipole moment is satisfactory. The charge density is compared with that calculated for  $CO_2$  by Mulligan (76).

The water and ammonia molecules have received attention over the last few years. Ellison & Shull (77) have carried out an SCF treatment for  $H_2O$  (45), all 10 electrons being considered explicitly; approximate values for some integrals were used. Calculations were carried out for various HOH angles at the observed OH equilibrium distance. The calculated dissociation energy is good. The change in the total molecular energy with angle is small (total range is 0.1 per cent between  $90^\circ$  and  $180^\circ$ ); the equilibrium value would be placed near  $120^\circ$  (obs.  $104\frac{1}{2}^\circ$ ). The dipole moment at  $105^\circ$  is calculated to be 1.52 D (experimental 1.84). Pople (78) has taken Ellison & Shull's expression for the MOs and converted them to localized symmetry orbitals. In this representation the two lone pairs are in a  $2p_z$  orbital and one which is primarily  $2s$  but involving sufficient  $2p_z$  so that it is directed away from the bonds. The latter makes the main contribution to the dipole moment. The two bonding orbitals make a contribution which almost cancels the proton moment about the oxygen nucleus. This shows how the total wave function

can be considered in different terms and equivalent orbitals might have been used with certain further advantages. Duncan & Pople (80) carried through an MO treatment of  $\text{H}_2\text{O}$  concluding that the lone pair electrons make a considerable contribution to the dipole moment. At the equilibrium angle, they break the moment of 1.84 D up into the following parts about the oxygen nucleus: lone pairs 3.03 D, bond electrons  $-6.82$  D, and protons 5.63 D. The division is approximately, though not exactly, that obtained from the Ellison-Shull functions.

Boys & Reeves (62) have made calculations for  $\text{H}_2\text{O}$  for seven nuclear configurations near the equilibrium one. They obtain an angle of  $96^\circ$ , smaller than the true one [contrast (77)] and a bond length about 5 per cent greater than that observed. The total energy is 99.1 per cent of the experimental, but the dissociation energy is only just over half the experimental value. The force constants have been obtained most impressively though the very small bond-angle interaction constant is given the wrong sign.

The  $\text{H}\cdots\text{H}$  distance in the isoelectronic  $\text{NH}_2^-$  in  $\text{KNH}_2$  (81) has been determined. For NH distances ranging from 1.00 to 1.04 Å the angle is calculated to be between  $109$  and  $103^\circ$ , so that there is little difference from  $\text{H}_2\text{O}$ . In the radical  $\text{NH}_2$  in its ground state the angle is  $103^\circ$  and the bond length 1.025 Å (82). So with three unshared electrons instead of four the angle is approximately the same as in  $\text{H}_2\text{O}$  and in  $\text{NH}_2^-$ . On the other hand, the marked effect of adding an extra electron to the electronic system of linear  $\text{CO}_2$  is shown by the fact that the angle in  $\text{NO}_2$  is  $134\frac{1}{2}^\circ$  (83). The angle in  $\text{H}_2\text{Se}$  has recently been found to be  $91^\circ \pm 0.6$  ( $\text{H}_2\text{O}$ ,  $104\frac{1}{2}^\circ$ ,  $\text{H}_2\text{S}$ ,  $92.3^\circ$ ) (84). That in  $\text{H}_2\text{Te}$  has been given as  $89\frac{1}{2}^\circ$  but only by assuming the molecule to be accidentally a symmetric top so that there is only one adjustable parameter. The bond length and angle are not, therefore, independently determined (85).

Higuchi has carried out an SCF LCAO MO treatment of  $\text{NH}$ ,  $\text{NH}_2$ , and  $\text{NH}_3$  at various bond angles (86). The molecular orbitals found for  $\text{NH}$  are similar to those found for  $\text{CH}$  (87). For  $\text{NH}_2$  and  $\text{NH}_3$ , to show the effect of changes in angle, MO energy diagrams of the type used by Walsh (88) have been drawn. The shapes of the curves are similar but do not coincide for various reasons. For both  $\text{NH}_2$  and  $\text{NH}_3$ , Higuchi has plotted the lone pair, bond, proton, and total moments as a function of the bond angles. In these molecules and in  $\text{NH}$  the lone pair electrons make a substantial contribution to the total. For  $\text{NH}_3$  the general pattern of the separate moments is similar to that deduced by Duncan & Pople (80).

McKean & Schatz (89) have measured the intensities of the infrared bands of  $\text{NH}_3$  (and  $\text{PH}_3$ ). The results are transformed, in the usual manner, to bond moments ( $\mu$ ) and  $d\mu/dr$  for the NH bonds. The values derived for  $\mu$  are 1.0 and 0.5 D for the symmetric and degenerate vibrations respectively, and for  $d\mu/dr$  are 0.6 and 0.2 D/Å (the usual differences). By assuming that the orbitals follow (90) the motion of the H atoms completely, the change in lone pair moment with angle is computed. Using this assumption it is

concluded that  $\mu_{\text{NH}}$  is 0.7 D ( $\text{H}^+$ ) and  $\mu$  (lone pair) is 0.7 D. This is different from (86) and (80) in which the lone pair moment was bigger than the total moment being reduced by the bond contribution. A similar treatment was carried out for  $\text{PH}_3$ .

Cohen & Coulson (91) have examined  $\text{NH}_3$  from a somewhat similar viewpoint though the treatment is more detailed and orbital following is assumed to be only partial. They agree with Duncan & Pople (80) as regards the various contributions to the dipole moment and conclude that the intensity of the symmetrical bending motion is a result largely of changes in the lone pair electrons.

For some time there has been interest as to why the bond angles in  $\text{NH}_3$  are near the tetrahedral values while those of  $\text{PH}_3$ ,  $\text{AsH}_3$ , and  $\text{SbH}_3$  approach more and more closely to  $90^\circ$  (cf. also  $\text{H}_2\text{O}$  to  $\text{H}_2\text{Te}$ , see earlier). Mellish & Linnett (92) have ascribed this to an electronegativity effect. This problem has been discussed more recently by Kolos (93) and by Mulliken (94). The latter suggests that *d*-hybridisation may be important in phosphorus which seems to be equivalent to saying that the phosphorus atom is more polarisable than the nitrogen atom. The explanation would not account for the angles decreasing towards  $90^\circ$  (though see  $\text{H}_2\text{Te}$  earlier). Mulliken states that "LCAO theory suggests that this factor may be somewhat fortuitous."

McDowell (95) has discussed the ionisation potentials of  $\text{NH}_3$ . The first appears to be at 10.1 eV (96) and the second at 15.31 eV. Wheland & Chen (97) by considering  $\text{NH}_3$  and  $\text{HN}=\text{NH}$ , have investigated why it is possible to obtain geometric isomers of  $\phi\text{N}=\text{N}\phi$  but not optical isomers of  $\text{NR}_1\text{R}_2\text{R}_3$ . They conclude that the *cis* to *trans* activation energy of  $\text{HN}=\text{NH}$  would be 33 kcal./mole. In the transition state complex one H atom is on the line of the two nitrogen atoms and the other HNN angle is  $76^\circ$  (97).

Using flash photolysis of mercury dimethyl, Herzberg & Shoosmith (98) have obtained absorption spectra of  $\text{CH}_3$  and  $\text{CD}_3$ . A band of the latter at 2140 Å is resolved and shows an intensity alternation. This would not be observed if the inversion doubling were small, i.e., if the molecules were far from being planar. It will be observed either if the molecule is planar or if the barrier separating the two minima is small so that inversion doubling is large. It has been suggested that the single lone electron will cause methyl to be pyramidal (88, 99). If this is so, the barrier will be smaller than in  $\text{NH}_3$  which involves two lone electrons and the doubling would be expected to be large. Higuchi (100) has reported briefly on calculations for planar  $\text{CH}_3$ .

Mashima (101) and Kisliuk (102) have discussed the dipole moment, bond angles and quadrupole coupling coefficients of  $\text{NF}_3$ , the small moment of which is interesting (103). They have presented varying descriptions involving hybridisation of the nitrogen and fluorine orbitals and ionic character of the NF bond. Difficulties arise because there are insufficient data to differentiate between the relative merits of alternative ways of describing electron shifts in the molecule.

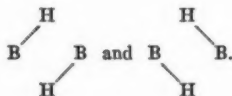
Carter (104) has treated  $\text{CH}_4$  and  $\text{SiH}_4$  using only wave functions centred

on the central atom thus avoiding the many centred integrals of the more conventional MO treatments. He obtains satisfactory values for the energies, bond lengths, and force constants. As regards the latter, consideration of the series  $\text{BH}_4^-$ ,  $\text{CH}_4$  and  $\text{NH}_4^+$  (105) and  $\text{AlH}_4^-$ ,  $\text{SiH}_4$  and  $\text{PH}_4^+$  (106) would have been interesting. A theoretical treatment of  $\text{CH}_4^+$  should be profitable, for Stevenson & Schissler (107) have shown that methane has a proton affinity of greater than 5 ev.

The molecule  $\text{O}_3$  has been examined (108). Various approximations have been considered, such as treating only the  $2p$  electrons or only the  $2s$  and  $2p$  electrons and using different forms for the AOs. It is found that some of the results are dependent on the type of approximation used. The calculations indicate that  $\sigma-\pi$  interaction is not negligible (109). The force field of this molecule has been studied (110).

Goldstein & Bragg (111, 112), using measurements of quadrupole coupling to determine bond character in the vinyl halides, showed that the number of  $p$ -electrons lost because of double bond character in the CX bond is 0.06 for the chloride and 0.03 for the iodide. The CCl bond shortening of 0.07 Å had been used to deduce a double bond character of 18 per cent whereas the dipole moment compared with that of ethyl chloride indicated 7 per cent (113). Goldstein (114) has carried out an MO treatment of the four  $\pi$  electrons in vinyl chloride and deduces 0.063 for the electron defect on the chlorine atom; the overlap population in the CCl bond is only 0.0224. The calculated ionisation potential was 9.99 compared with observed 9.95 ev (115).

*Some special systems.*—Hamilton (116) has carried out an SCF MO treatment of the four bridge electrons of  $\text{B}_2\text{H}_6$ , the contributing boron orbitals being restricted in their form. The gross atomic population (48) led to residual charges on the H atoms of  $-0.22e$ , agreeing with experimental conclusions (117, 118). Hamilton gives diagrams of electron density contours and considers what other more simple wave function would describe the system in a manner closest to the SCF MO description. He concludes, in a most interesting discussion, that one in which the two electron pairs are in two three centre orbitals is the best, being better than a resonance hybrid of two structures corresponding to



Lipscomb (119) has considered simplified LCAO models of  $\text{B}_5\text{H}_9$  and  $\text{B}_5\text{H}_{11}$ ; the former is known to have a large moment (2.1 D). He also examined the ground states of six electrons in a hemispherical box and shell, and concludes that such systems would have moments of 1.24 and 5.9 D though this would be reduced by electron repulsion. The electronic structure of an ico-

sahedron of boron atoms has been examined in relation to the possibility of the existence of  $B_{12}H_{12}$  (120).

Because there was no normal OH infrared band in  $Co(CO)_4H$  (121), it has been concluded (122) that the hydrogen atom is situated between three of the four carbonyl groups which form an approximately regular tetrahedron (123) and gives rise to a band at  $704\text{ cm}^{-1}$ . An MO treatment of the bonding of the H atom in this bridge model has been given (124).

The structure of ferrocene has continued to be examined and discussed. The two rings have been found to rotate freely (125). Dunitz & Orgel considered the energy levels and orbitals (126) and this has been studied further by Yamazaki (127), using a simple SCF MO procedure. Linnett (128) has compared the alternative representations in terms of molecular and equivalent orbitals.

Charge transfer complexes (129) have received attention. Collin & D'Or have shown that when chlorine is dissolved in benzene, a band at  $526\text{ cm}^{-1}$  ( $Cl_2$  free 557) appears (130), so in the complex the chlorine molecule must be unsymmetrical (131). Ferguson (132) has shown that, when bromine and iodine are dissolved in benzene, most of the infrared bands of the latter are unaffected but two are enhanced in intensity, and conclude that the symmetry changes [contrast (133)]. Molecular interaction between hydrogen chloride and donor molecules having electrons in  $\pi$ -orbitals have been studied using freezing point diagrams (134).

The suggestion that  $f$ -orbitals are involved in the bonds formed by elements of high atomic number (135) has been examined by Coulson & Lester (136) for uranyl and related compounds. They conclude that  $f$ -hybrids are probably involved but that  $6f$  orbitals are more effective than  $5f$ . The angular distribution of hybrids involving  $f$ -orbitals has been given (137).

Wheatley (138) has pointed out that molecules involving 12 ( $C_2H_4$ ), 24 ( $CH_2:CF_2$ ) and 36 ( $C_2F_4$ ) valency shell electrons are planar but those involving two more than these ( $N_2H_4$ ,  $(NHMe)_2$ ,  $N_2F_4$ ) are nonplanar. Those involving two less ( $B_2H_4$ ,  $(CHO)_2$ ,  $N_2O_4$ ) are planar in the free state but, in the solid lattice forces may bring about twisting. In this respect it is interesting that  $CHO \cdot NH_2$  (18 electrons and isoelectronic with  $CH_2 \cdot CHF$ ) is planar (139), the HNH angle being  $120^\circ$  (140). Urea is also planar (141).

*Changes in electron distribution.*—The use of infrared intensities to study changes of electron distribution on distortion has been mentioned, and its application to  $NH_3$  and  $PH_3$  examined (89). Eggers has discussed (142) the anomalous intensities of the infrared bands associated with certain bending vibrations of ethylene in terms of the changes in the  $\pi$  bond occurring on distortion with consequent shifts of electronic charge (143). Related to this is a consideration of the bending vibrations of some substituted benzenes for which there is a frequency increase and an intensity decrease with electrophilic substituents (144). McKean (145) has considered the results for  $BF_3$ , electron shifts being discussed in terms of hybridisation changes. Other molecules that have been studied are  $C_2H_2$  and  $C_2D_2$  (146),  $H_2CO$  (147), and  $BrCl$



and ICl (148). Russell & Thompson (149) have noted that, for the valency vibrations of various NH groups, the ratio of the intensities of the first overtone to the fundamental ranges from unity in methylamines to about 60 in acetanilide, indole, and carbazole. Both the mechanical and electrical anharmonicity have been calculated and are discussed. It seems that the difference may lie in whether the nitrogen lone pair is part of a resonating system or not. Thompson & Steel (150) have found that, for the CN bands in a number of substituted benzonitriles the logarithm of the intensity is a linear function of Hammett's  $\sigma$  factor for the various substituents, so that band intensity correlates with chemical reactivity. Other examples of the correlation of Hammett's  $\sigma$  factor with physical properties have been discovered during the last year (151).

*Electron distribution.*—One disadvantage of using an antisymmetrized product of MOs is that it is difficult to visualise the associated electron distribution. In an attempt to meet this Mulliken has devised a procedure called "electronic population analysis" (48). For an MO  $c_r\chi_r + c_s\chi_s$  ( $\chi_r$  and  $\chi_s$  are AOs) the net atomic populations are  $Nc_r^2$  and  $Nc_s^2$  and the overlap population (152) is  $2Nc_rc_sS_{rs}$  where  $N$  is the number of electrons in the MO and  $S_{rs}$  is the overlap integral. Gross atomic populations ( $N(k)$ ) are obtained by dividing the overlap populations into equal parts and adding these to the net atomic populations (i.e.,  $N(k) = N(c_k^2 + c_rc_sS_{rs})$ ) (153). When several orbitals are involved summation is over all these and a figure can be given for the gross charge on any atom in a molecule and also for the gross occupation of any atomic orbital. From these, amounts of promotion can be given. Mulliken gives the electron configuration in CO as  $1s_C^{2.00} \cdot 2s_C^{1.49} \cdot 2p_C^{2.42}$ ;  $1s_O^{2.00} \cdot 2s_O^{1.86} \cdot 2p_O^{4.23}$ . There has been a transfer of 0.09 electrons from C to O and, in both atoms, a promotion from  $2s$  to  $2p$  orbitals.  $H_2O$  and  $H_2$  are also examined and the concepts of free and forced hybridisation (154) discussed. This method gives some idea of the electron distribution; however the two net atomic and overlap distributions are not by any means nonoverlapping, so that it is not easy to attach a simple physical meaning to the results described in this way.

For presenting an idea of the electron distribution the notion of *loge* introduced by Daudel *et al.* (155) has great merit, and it is possible to state how good the description is in any particular case. The idea may be illustrated by considering the first excited state of helium (triplet  $1s \cdot 2s$ ) (156). The space is divided into two parts. The probability  $P_1$  of finding only one electron in the first part is calculated; the similar  $P_2$  is calculated for the second part. The sum of these has an upper possible value of 2 and  $(2 - P_1 - P_2)/2$  is called the lack of localisation,  $\eta$ . For  $p$  electrons of the same spin  $\eta = (p - \sum P_i)/p$ . If for helium in the above state the space is divided by a spherical surface it is found that  $\eta$  is a minimum (0.07) when the radius is  $1.7a_0$ . If the space is divided by a plane through the nucleus  $\eta = 0.5$  so that division by a sphere is more successful for describing the system. For the triplet excited state  $2s \cdot 2p$  a plane ( $\eta = 0.22$ ) is more successful than the best



sphere ( $\eta=0.48$ ). In an excited lithium atom (157),  $1s \cdot 2s \cdot 2p$ , all electrons having parallel spins, the best division is by a sphere and a plane, the latter applying to the region outside the sphere.  $\text{Li}_2$  has also been treated (158). A particularly interesting case is that of two electrons with parallel spin in  $\sigma$  and  $\pi$  bonding orbitals between two atoms. For a plane through the two atoms  $\eta=0.29$ , but the best ellipse is much worse ( $\eta=0.43$ ). The merit of this procedure is that it gives a clear picture of how the electrons of each spin are distributed by dividing ordinary space into separate regions one for each electron. It also gives a measure of how good this division is. The notion of loge derives its success from the fact that electrons of like spin tend to keep apart (159), a feature firmly stressed by Lennard-Jones (79) and forming the basis of his suggestions regarding equivalent orbitals.

Daudel (155) has also calculated the difference in electron density at a point in the molecule and the density that would exist there if the densities due to the constituent atoms were superimposed without perturbation; increase in the density between two atoms corresponds to bonding.

The study, with high resolution, of proton magnetic resonance spectra and the observation of small changes in the position of absorption (chemical shifts) with change in bonding of the proton promises to provide valuable information regarding the differing electronic situations of protons in different molecules and in different places in the same molecule. Pople (160) has discussed this effect in  $\text{CH}_3$ ,  $=\text{CH}_2$ , aromatic  $\text{CH}$ , and  $\equiv\text{CH}$ , and the effect of hydrogen bonding has been studied (161). Bernstein & Schneider (162) have measured the shifts in a large variety of conjugated aromatic hydrocarbons and from the intensities and by deuterium substitution have been able to link particular lines to particular protons. The same has been carried out for pyridine and methyl pyridines (163). These results have been interpreted by Bernstein *et al.* (164) using a concept which had been developed to discuss the diamagnetic susceptibility of benzene (165). It is supposed that the magnetic field induces currents flowing round conjugating paths and that these produce secondary magnetic fields at the nuclei. It is found that this picture accounts beautifully for the various shifts observed in a dozen aromatic hydrocarbons. Chemical shifts of nitrogen have been mapped (166).

*Chemical reactions.*—Griffing *et al.* have investigated, by an MO procedure, the interaction between stable molecules and atoms. The examples studied are four electron systems, in singlet states. The reaction of two hydrogen molecules with interchange of partners is examined for the situation in which the transition state complex is a square (167). Of the two MOs occupied in the initial state, the energy of one rises as the molecules come together and, in the transition state, becomes a member of a degenerate pair. For the system to continue to the products in their ground states, this electron pair must pass from one to the other member of this degenerate pair. Detailed calculation shows that no minimum of energy exists for a square arrangement of  $\text{H}_4$  and Griffing and Maček conclude this is improbable as

the transition state for the reaction. Griffing & Vanderslice (168) have considered the linear  $H_4$  system and have also made an MO treatment of the  $H+H_2$  reaction (169). For the latter an activation energy of 8.76 kcal./mole is obtained if Walsh & Matsen's value for the energy of  $H_2$  is used (170). This agrees well with the experimental value of 5 to 10 kcal./mole. The activation energy obtained using the best simple MO calculation (i.e., without CI) for  $H_2$  is 22 kcal./mole. Griffing *et al.* (171) have also considered the interaction of a beryllium atom with a hydrogen molecule in a triangular arrangement to form linear  $BeH_2$  and also in a linear arrangement to form  $BeH+H$ . In both cases, there must be a transfer in the transition state of one electron pair from one degenerate MO to another before the system proceeds to the products. It is found that  $BeH_2$  is metastable in the linear form, the P.E. curve having a minimum but the minimum energy being greater than that of  $Be+H_2$ . A semiempirical study of the  $HHCl$  transition complex has been made (172). This system has also been studied by Sato (173) who obtained satisfactory agreement with experiment.

Cahill & Mueller (174) have made a study of the induction effect considering in particular the system  $C\equiv C=O$ . They reach the conclusion that the inductive effect is carried out by a field mechanism. Other investigations of reactivity in more complicated systems have been made (175).

Relatively simple systems that might repay study from the point of view of reaction kinetics are  $HO_2$ ,  $HCO$ , and  $CO+O$  among others. The radical  $HO_2$  is almost certainly important in many oxidation reactions and there is now more data available regarding its properties (176). The dissociation energy of an OH bond in  $H_2O_2$  is  $89\frac{1}{2}$  kcal./mole and that of the OH in  $HO_2$  is  $47 \pm 2$ . Since dissociation energies of OH bonds are usually about 100 kcal./mole it appears that the structure of  $HO_2$  cannot be regarded simply as  $H-O-O$  but perhaps involves a stronger OO bond than a single one [cf.  $O_2^-$  (177)]. More is also known about  $HCO$ . Flash photolysis has been used (178) and, in the ground state, it is bent with an angle of  $119\frac{1}{2}^\circ$ . The upper state is linear. The dissociation energy of  $H-HCO$  is 75 and that of  $H-CO$  (to H and CO in their ground states) 31 kcal./mole (179). This is the same situation as in  $HO_2$  though the length of the CO bond in  $HCO$  is 1.20 as against 1.21 Å in  $H_2CO$ . The  $CO+O$  reaction is another extremely interesting reaction about which there is considerable uncertainty experimentally. Some theoretical guidance might be most useful here (180).

**Conclusion.**—In 1955, a Molecular Quantum Mechanics Conference recommended unanimously that bodies supporting research be asked "to give special attention to the problem of providing more high speed computing facilities for use in molecular problems." Recent literature shows that an increase in such facilities is greatly needed. Even diatomic molecules involving elements of the First Short Period are many body systems which are inevitably complicated and must involve lengthy computation for a complete solution of sufficient accuracy. However, it should be remembered

that the results of such treatments may be difficult to interpret in general terms (48, 155).

Besides providing a further means of obtaining numerical values for molecular properties, molecular quantum mechanics should provide new ideas and viewpoints to guide experimental chemists in the general consideration of their results and in the development of their experimental studies in new directions. Modern molecular orbital theory has not been as generally successful in this respect as pre-war valence bond and resonance theory. The impact of the latter, particularly in the hands of Pauling, was very extensive. Practically all branches of chemistry were affected. It is, of course, inevitable that much of the detailed theoretical work must involve methods and techniques, and therefore probably language, that cannot be understood by the experimental chemist, but comparatively little seems to have been done by most theoreticians to interpret their ideas for the benefit of experimentalists, and particularly to put the ideas into words and concepts which are more generally understood. For example, when Rosen first included  $2p$ -type orbitals in the treatment of the hydrogen molecule it was stated that this was to take account of polarization. When hybridization is now used to take account of such effects (though it is now used in other ways) the word polarization is rarely used, with the result that hybridization assumes for many a magic and, therefore, unsatisfactory quality in cases where this is not necessary. Dewar (181) has shown most clearly how the concept of  $\pi$  molecular orbitals in benzene and other molecules can be of the greatest assistance to practicing organic chemists and Coulson (182) has presented the procedure and ideas of modern quantum mechanics in a form which makes them intelligible to a much wider public. But there is still an unfortunate lack of real understanding between theoretical and experimental chemists. This problem, as well as the acquisition of high speed computing machines, is in need of most serious consideration.

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## HIGH POLYMERS IN SOLUTION

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Lack of space has made it necessary to leave out certain topics. Rather than to include a discussion of adsorption of polymers on solid surfaces and their spreading in monolayers, it was considered preferable to give a somewhat more detailed analysis of a restricted field. For the same reason no mention is made of polymers which are of direct biological interest. This applies in particular to nucleic acids and nucleoproteins, although these are often discussed in relation to synthetic polyelectrolytes. All references to gels and membranes have likewise been omitted, the more so because a recent discussion (1) deals with membrane properties and because ion-exchange resins and membranes are reviewed elsewhere in this volume.

To facilitate the reading, the reviewer has, against his own inclination, adopted a division into sections which, it is realized, is both artificial and arbitrary. Few subjects are less amenable to such an analytical approach as that of polymer solutions, where every property is closely related to almost every other. The reader will find that subjects discussed in one section could equally well have been discussed in another. It is hoped that the division in sections will not create an impression of inter-independence which in reality does not exist.

The literature survey for this review was completed in January 1957 at a time when the December 1956 issues of some journals were not yet available to the author.

### MOLECULAR DIMENSIONS IN SOLUTION

*Excluded volume.*—Many polymer properties, especially those in solution, are intimately related to the problem of the statistics of molecular configurations. In a previous review in this series, Wall & Hiller (2) have discussed this problem in some detail. Since then, several authors have contributed further studies.

Teramoto *et al.* (3) consider a three-dimensional cubic lattice but compute only an upper limit for the molecular weight dependence of the mean square end-to-end distance. Fixman (4) uses the Rouse-Bueche model (see below) and arrives at a series expansion for the mean square end-to-end separation  $\bar{h}$  in terms of  $M^{1/2}$ , where  $M$  is the molecular weight. Krigbaum (5) uses the method first advocated by Flory (6), but introduces several refinements: (a) the gaussian radial density distribution of polymer segments assumed by Flory is replaced by a more realistic one; (b) the fraction of permissible configurations for molecules with a given value of  $\bar{h}$  is not averaged over all  $\bar{h}$ -values; and (c) it is no longer assumed at the outset that the probability for the occurrence of a given  $\bar{h}$  is related to that for a random flight distribution

simply by a scale factor. It is found that a positive volume effect sharpens the distribution of end-to-end separations, the physical interpretation being that in the random flight statistics there are few configurations corresponding to large  $h$ -values, while the volume effect causes too much interference in configurations having small  $h$ -values. A comparison with experimental data is made by means of a particularly sensitive function:

$$g = (\alpha^3 - \alpha^2)/M^{1/2},$$

where  $\alpha$  is Flory's expansion factor and is derived from the intrinsic viscosity. According to Flory's original treatment,  $g$  should be independent of  $M$ . According to the refined theory, however,  $g$  goes through a flat maximum in accordance with experimental data.

In previous years, attention has been focused in particular on the behavior of  $h^2/M$  as  $M$  goes to infinity. Krigbaum points out that this ratio may converge too slowly to permit the verification of the theory by experimental tests. In fact, Wall, Hiller & Atchison (7), applying a high-speed electronic digital computer to several types of lattice, come to the conclusion that the results are compatible with the view that  $h^2/M$  converges as  $M$  goes to infinity, but that this convergence is extremely slow. It is doubted whether the limiting value is ever approached closely in real polymer molecules. An approximate formula representing the data is

$$h^2 = (n - An^4)/(1 - A)$$

where  $n$  is the number of steps on the lattice and  $A$  a parameter depending on the type of lattice and varying from 0.63 for the face-centered cubic to 0.94 for the tetrahedral lattice.

Finally, attention is drawn to the work of Marchal, Wippler & Benoit (8) who show that the average square of the dipole moment is much less (if at all) affected by volume exclusion than the mean square end-to-end separation. A theory of Marchal & Benoit (9) relates the average square of the dipole moment to the degree of free rotation about successive bonds in the chain. Good agreement is found with experimental results over a considerable range of molecular weights.

*Properties depending on dimensions.*—The deviations from random flight statistics have a bearing on various properties. Peterlin (10, 11) discussed briefly the effect on hydrodynamic interaction and on dissymmetry of light scattering, while Hammerle & Kirkwood (12) indicated how to account for non-gaussian statistics in the theory for dielectric behavior (see below). Mention may be made also of Temperley's (13) semiquantitative entropy considerations, in which the restrictions to free rotation and the volume effect are discussed in connection with various data.

Rheological and light-scattering studies with particular emphasis on the theory of molecular dimensions have been made by several authors. Krigbaum & Carpenter (14) found that Flory's "constant"  $\phi$  in the relation between intrinsic viscosity  $[\eta]$  and root mean square radius of gyration  $R$ :

$$[\eta] = 6^{1/2} \phi R^3 / M$$

decreases appreciably with increasing temperature for polystyrene in cyclohexane. Shultz & Flory (15) published an extension of Flory's theory of molecular dimensions and viscosity to mixed solvents and found good agreement with experiment for polystyrene in mixtures of benzene and cyclohexane but much poorer agreement in methylethylketone-methanol or carbon-tetrachloride-cyclohexane mixtures. Chinai and co-workers (16, 17, 18) investigated poly(methyl, ethyl and n-butyl)methacrylates of various molecular weights in methylethylketone (MEK) and in mixtures of MEK and isopropanol. The behavior observed could be described by Flory's viscosity theory. The extent of agreement with the Brinkman-Debye-Bueche theory (19, 20) or the Kirkwood-Riseman theory (21) was found to depend on the solvent, but part of the discrepancy between the experimental results and these theories was attributed to the manner in which the parameters occurring in the theoretical formulae are derived from the exponent  $\alpha$  in the modified Staudinger equation:

$$[\eta] = KM^\alpha.$$

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According to Varadaiah (22) the size of polyvinylacetate molecules in benzene, as calculated from viscosity according to the Flory-Fox theory, is about 50 per cent higher than that derived from light-scattering dissymmetry. Mention may be made also of Fuchs' measurements (23), who found that in solvent-precipitant mixtures  $[\eta]$  is not always a monotonic function of the solvent composition. In these experiments, no independent data were obtained for the solvent power of the mixtures.

The measurements of Hunt *et al.* (24) on cellulose trinitrate in ethyl acetate have led the authors to conclude that these molecules deviate considerably from random flight statistics and from spherical overall-shape. This is attributed to chain stiffness, a conclusion reached also by Levi *et al.* (25) for cellulose acetate. In this connection, mention is made of the work of Moore & Epstein (26) on the viscosity of cellulose nitrate in various solvents. Hunt and co-workers, using a formula given by Benoit & Doty (27) derive the so-called "persistence length" in the cellulose trinitrate chain as introduced by Kratky & Porod (28). The result, 117 Å, is in good agreement with the data of Holtzer, Benoit & Doty (29), and in reasonably good agreement with the value of 75 Å derived from small angle x-ray scattering by Kratky & Sembach (30, 31).

An extensive analysis of solution properties in relation to molecular dimensions has been given by Peterlin (32), who points out that in the Brinkman-Debye-Bueche theory (19, 20) expressions are derived for sedimentation rate and viscosity in terms of the hydrodynamic molecular radius  $R_H$  and the monomer radius  $b$  without making any assumption as regards the functional relationship between  $R_H$  and  $M$ . It is, therefore, possible to derive  $R_H$  and  $b$  independent of any assumption, to compare  $R_H$  with the radius  $R_L$  derived from light scattering and to study the relation between  $R_H$  and  $M$ .

In several cases examined, the agreement between  $R_H$  and  $R_L$  is excellent; the relation between  $R_H$  and  $M$  shows appreciable deviation from that required by random flight statistics. Interestingly, for polymethylmethacrylate in acetone, the hydrodynamic permeability increases with increasing  $M$  as a result of the non-gaussian statistics. The success of the Flory-Fox theory is attributed to the fact that the interval of  $M$ -values in which  $R_L$  is accessible to direct experiments is such that the change in permeability is small.

**Branching.**—For technical reasons much interest has been shown in branching. It is obvious from these studies that branching is often a disturbing factor in fractionation, as could be expected. Bier & Krämer (33), for instance, found that highly branched polyvinylchloride may have a higher intrinsic viscosity than a less branched sample of the same number average molecular weight.

An exhaustive review of the literature on polystyrene solutions by Hahn, Müller & Webber (34) revealed large discrepancies between the many  $[\eta]$ - $M$ -relations reported. These have often been attributed to differences in degree of branching, but the authors' own careful measurements do not reveal any significant differences between samples prepared under different conditions. On the other hand, Jones *et al.* (35) reported light-scattering results for polystyrenes with different degrees of branching and found good correlation between size and structure predicted from the conditions of synthesis. A similar discussion of branching and of grafting was given by Jones (36). Eriksson (37) found different relations between sedimentation constant  $s$  and molecular weight  $M$  and between  $[\eta]$  and  $M$  for samples of polymethylmethacrylate formed at different degrees of conversion. Flory's expansion factor for  $[\eta]$  appears to be different from that for  $s$ . Branching is mentioned as a possible reason for these discrepancies.

A fundamental study of branching was contributed by Brini & Benoit (38), who synthesized molecules of the type  $(R)_2C(OH)X$ , where  $R$  is  $C_{16}H_{33}$  and  $X$  is any of the following groups:  $CH_3$ ,  $C_2H_5$ ,  $C_4H_9$ ,  $C_7H_{15}$ ,  $C_{16}H_{33}$ . The intrinsic viscosities  $[\eta]$  of these branched molecules show a minimum value when  $X = C_4H_9$ . Calculations of the molecular dimensions show that there is a complete parallel between  $[\eta]$  and the radius of gyration.

The effect of branching on the dissymmetry of light-scattering was discussed by Benoit (39).

An interesting theoretical study by Kuhn & Majer (40) deals with crosslinking in solutions of such low concentration that only intramolecular links are formed. The effect on viscosity is discussed. This problem is of some interest in connection with  $\gamma$ -irradiation of polymer solutions, which sometimes gives rise to gelation when the concentration is high, but to a lowering of the viscosity when the concentration is low. The latter phenomenon has been attributed to degradation, but it is pointed out that it may be due to intramolecular crosslinking. Experimental studies on the effect of intramolecular crosslinking of polysiloxanes have been made by Price, Martin &

Bianchi (41), who observe low exponents  $a$  in Eq. I, and small changes in  $[\eta]$  when going from a poor to a good solvent, as expected.

Hobbs *et al.* (42) find that Huggins' constant  $k'$  defined by

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c \quad \text{II}$$

increases with  $[\eta]$  for branched chains of polyvinylacetate in benzene, in agreement with previous results reported by Cragg & Manson (43).

Particular attention has, of course, been paid to isotactic polymers. Trementozzi (44) reports a linear relation between  $\log [\eta]$  and  $\log M_w$  for isotactic polyethylene, but a nonlinear one for high-pressure polyethylene. Duch & Küchler (45) confirm the linear relation for isotactic polyethylene, but find hardly any correlation between  $[\eta]$  and  $M_w$  in solutions of a high-pressure sample. Moore's results (46) point also to pronounced branching and a very broad molecular weight distribution in polyethylene, in accordance with earlier results of Roedel (47), Billmeyer (48), and Beasley (49). The large width of the  $M$ -distribution is confirmed by Weszlau (50).

It is interesting to observe that for isotactic polystyrene, Natta *et al.* (51) found the same  $[\eta]$ - $M$ -relation as for other polystyrenes. Similarly, Peaker (52) found that the size and the second virial coefficient of a very high molecular weight isotactic polystyrene as derived from light-scattering is completely in line with the data for other polystyrenes.

#### THERMODYNAMICS

Zimm & Lundberg (53) have compared the results of various thermodynamic theories of polymer solutions with the "clustering function" discussed by Zimm (54). In Flory's athermal theory the clustering function is zero, which means that clustering is exactly balanced by the excluded volume effect. The introduction of a finite coordination number is equivalent to introducing more clustering. Experimental results for the systems benzene-rubber, polystyrene-toluene, and collagen-water are discussed.

According to a theory developed by Isihara & Koyama (55), the second virial coefficient  $A_2$  of a polymer solution can be written as a product

$$A_2 = a_2(T)F(x) \quad \text{III}$$

where  $x$  is proportional to the square root of the molecular weight  $M$  and to the excluded volume parameter:

$$\beta = 4\pi \int_0^\infty dr \ r^2 \{1 - \exp[-\phi(r)/kT]\},$$

$\phi(r)$  being the potential energy between two segments at a distance  $r$  apart. In a suitable range of  $M$ -values:

$$A_2 = KM^{-\epsilon}$$

where  $\epsilon$  and  $K$  are constants. This is identical with Grimley's earlier result (56). The fact that  $A_2$  in Eq. III contains a factor depending on temperature alone is consistent with the notion that the theta point (temperature at which  $A_2=0$ ) is independent of  $M$ . However, as pointed out by Orofino (57),

this is no longer true when higher order terms are taken into account. Orofino's treatment is an extension of the Flory-Krigbaum theory (58) for the interaction of a pair of polymer molecules whose segment distributions are gaussian with respect to the center of gravity. The interaction parameters calculated from second virial coefficients on the basis of Orofino's theory are in good agreement with those derived from viscosities.

Interesting results based on the lattice model were obtained by Flory (59) for semiflexible chains. The free energy of mixing was found to contain a term depending on a flexibility parameter  $f$ . If  $f$  is sufficiently small, the free energy of mixing becomes positive, indicating that the mixture becomes unstable. This is a consequence of the difficulty of filling a considerable fraction of space with sequences of rod-like segments whose orientations are random with respect to neighboring sequences. There will, therefore, be a tendency to create ordered states. Application to rod-shaped molecules is made (60) by setting  $f=0$ . Here an orientation parameter accounting for parallel orientation is introduced and then determined by minimizing the free energy. The occurrence of phase separation phenomena is predicted and compared with the results of earlier theories of Onsager (61) and Ishihara (62).

The lattice theory of polymer solutions has been subjected to a renewed analysis by Krigbaum (63), who believes that Flory's original approach (64) is better than the refinements introduced by Huggins (65), Miller (66), Orr (67), and Guggenheim (68) to account for a finite coordination number. The validity of Krigbaum's statement that the simple Flory expression explains the data equally well as or better than the refined treatments is open to doubt. Bueche & Krigbaum (69) give lattice calculations for various ratios between the cell volume and the size of the solvent molecules, and come to the conclusion that the entropy of mixing is not much affected by this ratio. The entropy is further said to be quite insensitive to molecular flexibility, in disagreement with the results of earlier theories by Staverman (70), Tompa (71), and Münster (72), and with the more recent theory of Flory (59). Recent heat of dilution measurements by Schuurmans (73) in dilute solutions of polyvinylacetate in toluene are not in conformity with the formula of Flory but can be explained by that of Staverman. Reasonably good agreement was established also with the conformal solution theory of Longuet-Higgins (74) and with the theory of Prigogine and co-workers (75, 76). No indication was found in Schuurmans' work for a break in the heat of dilution vs. concentration curve as reported by Rinfret and co-workers (77, 78). In connection with these experiments on heats of dilution we mention measurements by Jenckel & Gorke (79) for polystyrene in four different solvents and by Amaya & Fujishiro-Kobe (80) for polyvinylalcohol in water. From later measurements of vapor pressure in addition to the heat of mixing, Schmoll & Jenckel (81) concluded that the system polystyrene-toluene is athermal, in conformity with previous results obtained by Bawn *et al.* (82). The free energy cannot be explained by the Miller-Guggenheim formula,



but obeys the Flory-Huggins equation. This is a particularly clear example of a case where the  $c^2$ -term added by Huggins finds its origin entirely in entropy effects. This question is discussed also by Bawn & Wajid (83) for polystyrene in acetone and in chloroform. The same authors (84) report osmotic pressure data for polystyrene and polyisobutylene, and discuss the Flory-Fox theory in connection with viscosity data for these polymers (85).

The results obtained by Schmoll & Jenckel (81) for the system polystyrene-cyclohexane were applied to phase separation phenomena by Jenckel, Schmoll & Butenuth (86). Phase separation in solutions containing mixtures of polymers was investigated by Kern (87) who found only a rough correlation with cohesive energy densities. The results were discussed in terms of chemical structure. Two-phase systems of a different kind (one polymer in two immiscible solvents) were studied by Dobry (88).

Finally, some miscellaneous work on thermodynamics may be mentioned. Chang & Morawetz (89) published a spectroscopic and osmotic study of the association of polymers containing carboxyl groups in nonpolar solvents and came to the conclusion that most of the association is intramolecular. High precision ebulliometry of polyethylene in toluene, carbon tetrachloride and *n*-octane was reported by Smith (90). An interesting study of freezing point depression in cross-linked gels was carried out by Kuhn and co-workers (91, 92, 93). This work deals with the effect of the network on the size of crystals growing in the gel.

#### RHEOLOGY

*Viscosity.*—The anomalous behavior of  $\eta_{sp}/c$  at low concentrations  $c$ , which was discussed in a previous review (94) has been the subject of several studies. Öhrn (95) called attention to the effect of polymer adsorption on the effective diameter of the capillary in capillary viscometry. The importance of adsorption for dilute solution measurements has been confirmed by Fendler, Rohleder & Stuart (96) and by Takeda & Endo (97), who elaborated on Öhrn's technique to correct for it and suggested that the difference in behavior between branched and unbranched polyvinylchloride reported by Batzer (98) results from a difference in adsorption. Tuijnman (99) found similar results, but observed in addition that the non-Newtonian character of the flow may have a quite pronounced effect: the anomaly disappears when corrections for non-Newtonian flow are made.

*Non-Newtonian and visco-elastic behavior.*—The effect of shear-rate  $\dot{q}$  on intrinsic viscosity  $[\eta]$  has often been determined by simply extrapolating  $(t-t_0)/t_0c$ , where  $t_0$  is the efflux time for the solvent and  $t$  that for the solution at concentration  $c$  and at the same driving pressure. It can be shown that this is not permissible (e.g., 100), and although Golub (101) has demonstrated that the error involved is small for polyisoprenes in benzene, this is not true for polyvinylacetate in toluene (99). The danger inherent in the extrapolation procedure is demonstrated particularly clearly by the work of Goldberg & Fuoss (102), who showed that the data of Staudinger & Sorkin

(103), which were used by Kuhn (104) to support his theory, do not in reality show any significant effect of  $q$  on  $[\eta]$ .

A second problem is that of the behavior at low gradients. From the simple physical argument that the shearing stress  $\eta q$  must change sign with  $q$ , one arrives at the inevitable conclusion that  $\eta$  is an even function of  $q$ . Some indications for this were found by Fujita & Homma (105), but stronger evidence was given by Wada (106), Katchalsky & Sternberg (107), Alexander & Stacey (108), Čopič (109) and Tuijnman (99). Yet, the majority of workers in this field have published data which suggest an uneven function at low  $q$ -values. We mention by way of example: Sharman *et al.* (110), Flory (111), Maclay & Fuoss (112), Goldberg & Fuoss (102), Patat & Hartmann (113), Golub (114), Claesson & Lohmander (115). In Golub's work the gradient  $q$  was as low as  $1 \text{ sec}^{-1}$ , while Claesson, who used an ingenious optical device to follow the meniscus, reached  $q$ -values less than  $0.2 \text{ sec}^{-1}$ . The pronounced upward curvature in the  $\eta$ - $q$ -relation which these authors found at low gradients must perhaps be attributed to the occurrence of a kind of yield value, similar to that observed by Pals (116) and attributed by him to the advancing meniscus in the second leg of the (Ostwald) viscometer.

On the other hand, this upward curvature was predicted by Bueche (117) who derived the relation

$$[\eta]_q = [\eta]_0(1 - aq^{1/2})$$

on the basis of a simple molecular model. This model consists of a string of beads connected by Hookean springs and will in the following be referred to as the Rouse-Bueche model (117, 118, 119). It must be remarked, however, that Bueche's calculation is only approximate; Zimm's (120) more rigorous treatment of the same model predicts Newtonian behavior. Moreover, it is claimed by Peterlin & Čopič (121) that although certain data appear to confirm Bueche's formula, these data do not completely rule out other  $\eta$ - $q$ -relationships.

The failure of Zimm's calculation to yield non-Newtonian intrinsic viscosity is due to the fact that the tensor character of the frictional resistance was ignored. Kuhn & Kuhn (104) in their treatment of the elastic dumbbell model introduced this explicitly by pointing out that as a result of potential barriers opposing the free rotation around C—C linkages, the resistance experienced when the vector  $h$  joining the endpoints of the molecule is changed at a certain rate is larger for movements in the direction of  $h$  than for movements perpendicular to  $h$  ("internal viscosity" or "shape resistance"). Čopič (109) observes that this is true even in those cases where the internal viscosity is negligible, because the hydrodynamic interaction for motions in the direction of  $h$  is different from that for motions perpendicular to  $h$ . This is worked out on the basis of the Kirkwood-Riseman theory (21), although the model used eventually by Čopič is Kuhn's elastic dumbbell model. Two different attempts to introduce shape resistance in the application of the Rouse-Bueche model were made by Cerf (122) and by Van Beek (123). A

rigorous theory of the visco-elastic and the non-Newtonian behavior of rod-shaped particles was worked out by Kirkwood & Plock (124).

Of the experimental data on visco-elastic properties we mention those published by Landel & Ferry (125). These show a spectrum of relaxation times that is much flatter than that predicted by Rouse (118). This discrepancy is attributed to interaction between the polymer molecules.

*Flow birefringence.*—Cerf's earlier work (126) on flow birefringence was based on the model of a deformable sphere. Some relations derived in this work were rederived more recently (127) by different methods. At the same time an explanation was given of the failure of the extinction angle to approach zero when the gradient  $q$  becomes very large, which was formerly explained by polydispersity [Sadron (128)]. Furthermore, Cerf (129) has elaborated on the earlier results for the relation between extinction angle and solvent viscosity, and has indicated how to include internal viscosity in the treatment of the Rouse-Bueche model.

Čopič's (130) treatment of flow birefringence is based on the introduction of hydrodynamic interaction as described above in the subsection on viscosity. Moreover, he takes into account not only the intrinsic anisotropy of the chain segments, but also the electrical interaction of these segments which gives rise to what may be called form birefringence. This enables him to explain the parabolic dependence of flow birefringence  $\Delta n$  on gradient  $q$  found experimentally by Cvetkov (131) for polystyrene in dioxane:  $\Delta n$  is positive at low gradients, passes through a maximum when  $q$  increases and eventually becomes negative.

*Dielectric losses.*—In Van Beek's work (123, 136) use is made of the Rouse-Bueche model with free draining, assuming beads carrying charges alternating in sign in order to represent a succession of dipoles. The assumption of free draining is based on the intuitive reasoning that the hydrodynamic interaction is caused by the forces exerted on the beads which in turn transfer these forces to the liquid. Since the forces acting on successive beads are equal but opposite in sign, we may expect that their effect at some distance from either of them is quite small. This is borne out by Zimm's work (120) where it is shown that the hydrodynamic interaction is of little consequence. The result of the calculation is a loss curve with a single relaxation time which is independent of molecular weight  $M$ . This independence is confirmed experimentally by the results of De Brouckère and co-workers (132, 133).

On the other hand, Hammerle & Kirkwood (12) have introduced hydrodynamic interaction into the earlier treatment of a more realistic model by Kirkwood & Fuoss (134), and have come to the conclusion that the frequency of maximum loss should be inversely proportional to  $M^{1/2}$ , when the chain is gaussian, and to  $M^p$  with  $p > \frac{1}{2}$  when the effect of the excluded volume is taken into account. In later work Hammerle & Kirkwood (135) have shown that their theoretical loss curve is only slightly broader than Van Beek's experimental one. The fact that the frequency of maximum loss is independent of  $M$  is attributed to molecular interaction. The necessity of

working at high concentrations has always been a severe restriction in dielectric studies. In the work of Hartmann & Jaenicke (137) the lowest concentration is as high as 18 volume per cent. Their results are of interest in that they seem to show a measurable effect of molecular orientation in a field of flow on the dielectric constant of the solution.

The results of Allg n (138) on the dielectric losses in polyelectrolyte solutions are probably best explained by relaxation effects in the electric double layer.

*Concentrated solutions.*—In a recent extension of his earlier theory (139), Bueche (140) made an attempt to explain why the viscosity of very concentrated solutions and of polymers in bulk is proportional to  $M^{2.5}$ .

An interesting approach to concentrated solutions subject to a shear-rate was published by Lodge (141). His work is based on the model of a network with temporary crosslinks to which an average life-time is attributed, and the assumption is made that birefringence and tension are determined by the momentary state of the network, so that the relation between birefringence and tension is the same as that for crosslinked rubber (142, 143, 144). Severely restricting is the assumption that the number of crosslinks is independent of the gradient, but this can perhaps be amended by incorporating the ideas developed long ago by Goodeve (145). Lodge's theory has been confirmed experimentally by Philippoff (146). An entirely different approach to concentrated solutions was made by Bestul (147) in his theory of shear degradation, in which a formal analogy with thermal degradation is assumed.

*Miscellaneous.*—Lifson (148) calculated the effect of the inhomogeneity of capillary flow on the apparent specific and intrinsic viscosities. Daune *et al.* (149) discussed the use of diffusion for the study of polydispersity. Absorption of sound waves was studied by Cerf & Laville (150). A theoretical discussion of the effect of a transverse electric field on the viscosity was given by Peterlin (151). Fujita (152) developed a theory of centrifugation for cases in which the sedimentation coefficient is concentration dependent. Infrared flow-dichroism was discussed by Bird & Blout (153).

An interesting micromethod of measuring diffusion rates was indicated by Nishijima & Oster (154), who showed that the local ("microscopic") viscosity of the solution is much lower than the macroscopic viscosity when the polymer concentration is low. From a certain concentration onwards the microscopic viscosity increases rapidly with increasing concentration. The results were confirmed by measurements of fluorescence.

Martin *et al.* (155) used sedimentation in water and in heavy water to determine the partial specific volume of the solute. This is based on the assumption that the solvent-solute interaction in these two solvents is the same. A suggestion to use the Huggins equation II for the determination of intrinsic viscosities when the polymer concentration is unknown was made by Frisch & Jung Yeh (156).

Finally, mention is made of experiments on thermal diffusion of various polymers in water by Langhammer (157) and of polystyrene in various sol-

vents by Emery & Drickamer (158). The latter authors develop an equation for the Soret effect and find it confirmed by experiment. It is found that fractionation by thermal diffusion, if at all possible, can be achieved only at low concentrations.

#### LIGHT SCATTERING

A contribution to the problem of absolute turbidities of pure liquids, which was discussed in a previous review (94), has been made by Cantow (159), who confirms the high values first found by Carr & Zimm (160) and attributes the low values to the neglect of refractivity corrections. In this connection, mention is made of the accurate results for pure water obtained by Kraut & Dandliker (161). These authors studied also the secondary scattering in ludox solutions (162) and gave a theoretical discussion of this phenomenon.

The work of Benoit (163), dealing with the effect of polydispersity on the dissymmetry of light scattering by coiling chain molecules, was extended to rod-shaped particles by Holtzer (164). A theoretical study of the effect of optical anisotropy of the polymer segments on the determination of particle size was made by Benoit (165, 166), who concluded that this effect is usually quite small. A more complete treatment of the light-scattering by anisotropic particles can be found in Horn's thesis (167), where in addition some experiments with tobacco mosaic virus, cellulose nitrate and thymonucleic acid are discussed.

A theoretical treatment of light-scattering by chain molecules whose segments are oriented by an external electric field was given by Isihara *et al.* (168), who restricted the calculation to optically isotropic segments. A more general theory both for rods and for coils was developed by Wippler (169) as a continuation of work discussed in a previous review (94). The change in the angular scattering function  $P(\theta)$  was found to be proportional to the square of the external field. Furthermore, rather large effects of polydispersity are to be expected. The theory was confirmed experimentally for tobacco mosaic virus in water, polyphenylalanine in benzene, and cellulose nitrate in ethyl acetate. The failure to find any effect in solutions of polystyrene or polymethylmethacrylate was attributed to the fact that in these molecules the dipoles are situated in the side-chains and, therefore, contribute little to the deformation of the chain molecule as a whole.

Cantow (170) used light-scattering at different temperatures to obtain heats and entropies of dilution. In some of his measurements white light was used to increase the intensity. For particles which are small compared to the wavelength of light this is permissible if the calibration is made with a known polymer. For larger particles it is necessary first to extrapolate to zero scattering angle where  $P(\theta)$  equals unity. Schulz *et al.* (171) have likewise used light scattering to derive thermodynamic data for natural rubber in cyclohexane.

## POLYELECTROLYTES

*Binding of counterions.*—The theories of Katchalsky & Lifson (172) and Hermans & Overbeek (173) on molecular dimensions and thermodynamics of polyelectrolytes in solution rely on the Debye-Hückel approximation, which assumes low electric potentials. Attempts to avoid this approximation have so far not been very successful. Several authors have, therefore, taken recourse to ion-binding, without necessarily specifying that this must be taken literally or as a substitute for the formidable mathematical difficulties one encounters when the electric potentials are appreciable. This approach is similar to that applied to micellar soap solutions (174 to 177).

Rice & Harris (178) introduced ion-binding and used the one-dimensional Ising lattice to account for interaction between nearest and next nearest neighbors. The method was applied also to polyampholytes (179), with either a regularly alternating structure or a random distribution of positive and negative groups. The conclusions reached are, among other things: (a) ion-binding does not cause a large change in the titration curve if there are appreciable numbers of both positive and negative charges, but diminishes the degree of ionization when the charge is predominantly of one sign; (b) added salt shifts pH towards the isoelectric point; (c) the buffering capacity of a random acid-base copolymer is greater than that of a regularly alternating one; (d) the molecular dimensions of a polyampholyte at a given pH do not depend strongly on salt content; (e) in salt solutions, the inside of a polyion is nearly neutral, so that the interaction between two polyions is governed primarily by their spatial dimensions (see also Orofino's method below). The application of the ion-binding concept to polyelectrolyte gels and ion-exchange resins (180) lies outside the scope of this review.

Orofino's extension of Flory's theory mentioned in the section on thermodynamics was applied by him (57) also to polyelectrolytes in salt solutions. Each polymer molecule is described by a gaussian distribution of segments, and each volume element within the molecule is considered to be electrically neutral and in Donnan equilibrium with the external solution. In any region where two polyions overlap, the density of charges fixed on the polymers is increased, thereby increasing the Donnan free energy. Essentially, it is this change in local Donnan free energy that is responsible for the "electrical" part of the second virial coefficient. The free energy found agrees qualitatively with experimental results but indicates once again that quantitative agreement can be reached only if an effective charge is introduced, which is considerably less than the real charge of the molecule.

A distinction between strongly and weakly bound ions was made by Wall and co-workers (181) on the basis of transport numbers as a function of current-density. The results agree roughly with conclusions drawn from viscometry (182). Similar results were obtained by Inagaki *et al.* (183, 184): the second virial coefficient derived from osmometry is a linear function of the reciprocal ionic strength [cf. Pals (185)], but the slope is smaller than that required by the Donnan equilibrium as a result of the fact that only a



fraction of the molecular charge is effective. Similarly, the intrinsic viscosity obeys the Hermans-Overbeek theory (173) provided an effective charge is introduced.

A different approach to the problem of counterion activity, which avoids the concept of ion-binding, was suggested by Kagawa (186), who replaced the Poisson-Boltzmann equation by a linear interpolation formula which represents a reasonably good approximation for  $(\phi/kT)$ -values between 0.5 and 2.

In connection with ion-binding mention is made of the potentiometric titration of polyacids in the presence of divalent ions by Gregor and co-workers (187). The complexing of copper ions with polyacids was studied by Morawetz *et al.* (188, 189) using titration, absorption spectra, and dialysis equilibria.

*Dimensional properties.*—It appears to be well established that the maximum observed in  $\eta_{sp}/c$  when a polyelectrolyte is diluted at constant salt content occurs also in pure water at a very low concentration of the polymer. According to Jordan *et al.* (190) this is true both at high and at low shear-rates. The polymer investigated was poly-N-butylvinylpyridiniumbromide (PVB). Jordan reported also sedimentation rates and extinction angles. A plot of extinction angle vs.  $(\eta - \eta_0)q/c$  where  $q$  is the gradient was found to be the same for different concentrations, in accordance with results obtained by Peterlin (191). This was not confirmed, however, by Mathieson & Porter (192), who measured extinction angles in solutions of sodium alginate.

In earlier work of Fuoss & Strauss (193) it was found that  $[\eta]_{\infty}$ , i.e.,  $[\eta]$  at the limit of high salt content for PVB in salt solutions, depends only on the counterion. Kagawa & Fuoss (194) showed, however, that for polyacrylates  $[\eta]_{\infty}$  depends also on the by-ion.

Arnold & Caplan (195) determined the size of polymethacrylate ions by light scattering and found that the Hermans-Overbeek theory (173) describes the effect of the ionic strength but underestimates the variation with degree of dissociation. Terayama (196) compared different dilution techniques in the presence of salt: iso-ionic, constant salt content, constant polymer to salt ratio, and constant counterion content. The results are in agreement with previous work of Pals (116) and Terayama & Wall (182).

From the angular dependence of light scattering by polymethacrylate, Alexander & Stacey (108) conclude that the molecules are stiff, highly swollen coils. The non-Newtonian behavior of these molecules follows the predictions of Kuhn when the molecular weight is of the order of  $10^6$ , but when  $M$  is ten times as large the molecular interaction becomes predominant. Viscosity studies on xylanmethyluronate from jute were published by Das Gupta (197), and on gum tragacanth by Basu & Sircar (198). These authors obtained the usual type of  $\eta_{sp}/c$  vs.  $c$  curves for polyelectrolytes. Winter & Beckmann (199) described their viscosity results for carboxymethyl polysaccharides by a new empirical equation.

A curious result was obtained by Contois & Trementozzi (200), who



found that the  $\eta_{sp}/c$  vs.  $c$  curve for polymethacrylate in the presence of bivalent anions showed upward curvature on dilution, as in pure water. Studies on sedimentation of carrageenane at various temperatures were made by Goring & Chepeswick (201), and on diffusion of polymethacrylate in water by Kedem & Katchalsky (202). The diffusion results indicate a rod-like shape at high degrees of ionization  $\alpha$ . When  $\alpha=0$ , the diffusion coefficient can be calculated quite well from the Kirkwood-Riseman theory (21) if the effective bond length is derived from  $[\eta]$ .

The viscosity changes observed when going from a polyelectrolyte to a polysoap are described by Strauss *et al.* (203). Aggregation of the hydrophobic chains attached to the same polymer molecule causes this molecule to reach a degree of compactness which ordinary polymers cannot assume without phase separation. This suggests that similar phenomena are to be expected in block- and graft-copolymers. The results suggest further the existence of a critical content of soap-groups, analogous to the critical micelle concentrations of ordinary soap solutions.

**Complex coacervation.**—In the extensive work of Bungenberg de Jong (204) on coacervates, complex coacervation is defined as reversible phase separation in systems containing electrically charged macromolecules. In Voorn's (205) mathematical description of this phenomenon the free energy of a solution containing polyelectrolytes and salts is written as the sum of the Flory-Huggins expression  $F_0$  and the term  $F_e$  derived for electrolytes by Debye & Hückel. All ions, including those fixed on the polymer molecules, are treated as independent monovalent ions. Since, for a given density of charges fixed on the polymer,  $F_e$  is a function of the volume fraction, whereas  $F_0$  depends also on the molecular weight, coacervation is favored by large  $M$ -values and by the addition of solvents which lower the dielectric constant. The prediction that the concentration of added salt is slightly larger in the coacervate than in the equilibrium solution was confirmed by experiment. This unequal partition of the salt explains why salt can impede the occurrence of complex coacervation.

**Electrophoresis.**—When a sufficient amount of salt is present, polyelectrolyte molecules should behave as almost free-drained particles when subject to an external electric field. This is due to the fact that the hydrodynamic interaction between the segments results from forces exerted on the segments which in turn transfer these forces to the liquid. Since at high ionic strengths the charge density in any volume element of the molecule is practically equal to zero, the net force acting on a volume element is zero or at least very small, so that there is no hydrodynamic interaction. Under these circumstances the electrophoretic mobility should be independent of ionic strength and molecular weight, provided Debye-Onsager relaxation effects may be neglected. The independence of  $M$  is confirmed by experiments of Cook *et al.* (206) and of Goring (207) in solutions of carrageenin.

At lower ionic strengths the molecule becomes less free-drained. Fujita & Hermans (208) used an extension of the Brinkman-Debye-Bueche method

(19, 20), while Hermans (209) gave a treatment based on a simplified application of Oseen's equations to a porous sphere. The results obtained are essentially the same as those derived by Overbeek & Stigter (210), who write the electrophoretic velocity as the sum of three contributions:  $u_1$  due to that part of the fixed charge which is compensated by counterions inside the molecule,  $u_2$  due to the remainder of the fixed charge, and  $u_3$  due to the counterions outside the molecular domain. Each of these contributions can be derived immediately from known formulae.

The model used in these treatments was applied to the conductivity problem by Hermans & Fujita (211).

*Miscellaneous.*—According to Suzuki & Matsuda (212) the refractive index of aqueous sulphonated polystyrene at very low concentrations  $c$  is not proportional to  $c$ . A similar curious result was reported by Arnold & Caplan (195) for polymethacrylic acid.

Schindewolf (213) found anisotropy in the conductivity of polyphosphate solutions when subjected to a shear-rate.

Acid-base catalysis was studied by Morawetz & Westhead (214), who found that the reactivity of *p*-nitrophenyl ester groups in neutral solution is increased by a factor  $10^6$  when the groups are attached to a polyacid. On the other hand, the rate of basic hydrolysis of *p*-nitroanilide groups attached to a polyacid is very low. The pronounced acceleration of this hydrolysis by small amounts of barium ions is interpreted as attributable to chelation.

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# KINETICS OF POLYMERISATION<sup>1</sup>

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## INITIATION

Peroxy and azo compounds are widely used as initiators for polymerisation reactions. A knowledge of the rate of production of free radicals and of their efficiency in starting a polymer chain is required for the evaluation of the several rate constants.

Barson & Bevington (1) have applied tracer techniques to these problems. Benzoyl peroxide uniformly labelled with C<sup>14</sup> in all positions, and solely in the carbonyl group enable the finer details of the decomposition to be elucidated.



The thermal decomposition in benzene at 60°C. yields the theoretical quantity of CO<sub>2</sub>, but if diphenylpicrylhydrazyl (DPPH) is present in sufficient excess no gas is evolved. When carbonyl labelled peroxide (C<sub>6</sub>H<sub>5</sub>·C<sup>\*</sup>OO)<sub>2</sub> is used to initiate the polymerisation of styrene an active polymer is produced, and from intensity, and molecular weight measurements, it is estimated that 85 per cent of all chains are initiated by the benzoate radical. Decomposition of the peroxide in a transfer solvent, e.g., cumene, yields reduced quantities of CO<sub>2</sub>.

DPPH inhibits the polymerisation of styrene by azoisobutyronitrile, and using the velocity constant for this decomposition (2), Bevington (3) shows that one initiator fragment [CMe<sub>2</sub>(CN)·] combines with one hydrazyl radical during the induction period. The subsequent polymerisation at 60°C. is retarded by the products of radical interaction. The polystyrene produced is coloured and shows activity when C<sup>14</sup> labelled DPPH is used.

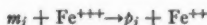
The stable free radical O·N(pC<sub>6</sub>H<sub>4</sub>·Me):C(Me)·CH<sub>2</sub>·C(Me)<sub>2</sub>·N(C<sub>6</sub>H<sub>5</sub>)·O· is, according to Bevington & Ghanem (4), a superior radical scavenger to DPPH. Investigations proved it to be thermally unstable, and suggested differing rates of initiation for styrene, and methyl methacrylate by azoisobutyronitrile. Kice (5) deduces from a study of several inhibitors in the systems; methyl methacrylate, or styrene and azoisobutyronitrile, that the efficiency varies for the two monomers. The results are explained in terms

<sup>1</sup> The survey of literature pertaining to this review was concluded in November, 1956.

<sup>2</sup> I am indebted to Professor G. M. Burnett for discussions concerning this contribution.

of the steric and polar effects concerned in the radical inhibitor interaction.

The use of ferric ions as chain stoppers is recommended by Collinson & Dainton (6). With sufficient excess of  $\text{Fe}^{+++}$  all chains in the polymerisation of acrylonitrile are terminated by the mechanism:



hence the rate of initiation can be deduced. This method is similar to that proposed by Bamford, Jenkins & Johnstone (7), utilising  $\text{FeCl}_3$  in nonaqueous solution. This work leads to values of 0.62 to 0.56 for the efficiency of azoisobutyronitrile, similar to other quoted values (7).

O'Driscoll & Tobolsky (8, 9) show that the use of benzoyl peroxide and dimethylaniline in a reduction activation system enables the polymerisation of methyl methacrylate to be studied over the temperature range 20 to  $-40^\circ\text{C}$ . The overall rate is given by the expression,

$$R_p = C([\text{Bz}_2\text{O}_2][\text{DMA}])^{1/2}$$

#### AUTOCATALYTIC AND GEL PHASE POLYMERISATION

It is tempting to assume that the increase in the rate of reaction in cases where the polymer is insoluble in its own monomer, and in the gel phase of homogeneous reaction, arise from a common effect. In each case, the rate of termination of growing chains is reduced, and recently it has been demonstrated that in these systems macroradicals can exist for a very long time. In the simpler homogeneous system, assuming the mutual destruction of growing radicals, the overall rate is proportional to the half power of the catalyst concentration, or the intensity of irradiation (gamma radiation or ultraviolet).

Values of this exponent reported for the polymerisation of acrylonitrile are 0.82, and 0.76 to 0.97 (10), for the catalysed reaction, whilst the range 0.76 to 0.95 is quoted for  $\gamma$  initiation (11). The wide spread in the latter values has been attributed to a nonhomogeneous distribution of initiating centres. Prevot-Bernas & Sebban (12) find the value of 0.76 to 0.79 for initiation in the bulk, and a more normal figure of 0.55 using dimethyl formamide as solvent. However, using water as solvent the values range from 0.25 to 0.95 with increasing water content, under conditions which were shown to be homogeneous for dimethyl formamide solutions.

Chapiro (13) has demonstrated the presence of a post-polymerisation amounting to 2 per cent polymerisation at 40 per cent conversion upon removing vinyl chloride from the  $\gamma$  source, the effect being detectable up to 20 hr. Magat (14) states that the effect is even more pronounced in precipitating acrylonitrile polymerisations, and is persistent for 100 days. Bamford & Jenkins (15) indicate that all these facts can be explained on the assumption

that macroradicals are trapped in the solid polymer thrown out of solution. Indeed, they can initiate further polymerisation in a violent and spectacular way (16). Further, these trapped radicals can be detected via their unpaired electrons in electron spin resonance studies (17).

Melville *et al.* (18), using improved nonstationary state methods, show that radicals having a half life of up to 100 sec. appear in the homogeneous polymerisation of vinyl acetate and methyl methacrylate. If this second monomer is polymerised in the presence of the bi-functional monomer glycol dimethyl methacrylate, a cross linked gel is formed, and the exponent rises from an initial value of 0.50 to 0.80, when the system sets to a glass and the reaction ceases (18, 19). If one in every three steps in the chain propagation is the addition of the bi-functional monomer, there is continuous rate acceleration up to 40 per cent conversion, when the reaction stops. It is estimated that this system then contains  $10^{-8}$  moles/litre of immobilised radicals which cannot propagate or terminate because of the glassy state of the reaction product. These radicals can also be detected by the electron spin resonance technique, and it is most interesting to note that Whiffen *et al.* have pointed out the identity between the spectrum found and that resulting from the  $\gamma$  irradiation of polymethyl methacrylate (20).

Onyon (21) confirms that the photoinitiated polymerisation of acrylonitrile follows a more conventional course when carried out in a polymer solvent. An exponent of 0.5 is found, but transfer to the solvent is significant.

Solid monomers were polymerised by Mesrobian *et al.* (22) using  $\gamma$  initiation. They estimate that radical concentrations of  $10^{-4}$  molar are frozen into polyacrylamide at  $-179^{\circ}\text{C}$ . The molecular weight of the polymer is constant over a 270-fold variation of radiation intensity. Several monomers show little or no change in reaction rate upon passing through the melting point. This is in direct contrast to a similar study by Lawton, Grubb & Balwit (23) using high energy electrons, and methyl cyclosiloxane.

#### BRANCHED, GRAFT, AND BLOCK COPOLYMERS

Interest continues to be shown in the preparation of these types of polymers. Copolymers can be made from monomers which will not undergo polymerisation using the more conventional method of mixed monomer feed.

Mechanical shear can fracture a polymer chain, and produce fragments with free radical ends. Henglein (24) shows that they can be detected by the radical scavengers DPPH, and iodine, and estimate that during the ultrasonic degradation of polystyrene and methyl methacrylate 40 and 20 per cent of all the radicals produced recombine. These two figures are in the same ratio as those for the estimated amount of combination when these two radicals are concerned in the termination step of a polymerisation reaction (25). Melville *et al.* (26) show that the ultrasonic degradation of these two

polymers in dilute solution results in block copolymer formation, presumably by means of a cross combination process. Angier & Watson (27), using a specially designed masticator capable of high rates of shear, show that natural rubber can be broken into free radicals which can then initiate the polymerisation of a second monomer previously imbibed in the rubber (28). The mechanism was examined in detail by using DPPH and S<sup>35</sup> labelled dimethyldisulphide as radical scavengers. Osmotic molecular weights, radiochemical assay, and spectrophotometry were used to determine the number of new polymer chains produced by mastication. Synthetic rubbers can be made to add to radical accepting monomers by this method, providing antioxidants and other impurities are removed prior to the mastication process.

Several chemical methods are available. Melville *et al.* (26) used *m* di-(hydroperoxy-isopropyl)benzene to initiate the polymerisation of styrene at 50°C. The resultant peroxy ended polymer is dissolved in methyl methacrylate monomer, emulsified, and the second block added by initiation with Fe<sup>++</sup>. Bamford & White (29) use a similar approach. First, methyl methacrylate is polymerised in the presence of a tertiary amine to produce an amino ended polymer by transfer; this polymer is then used as a transfer agent in the polymerisation of acrylonitrile at 60°C. The transfer constant for this process ( $k_{tr}$ ) is 0.52, compared with 0.59 for the corresponding reaction using triethylamine.

M. H. Jones (30) shows that polystyrene can be photobrominated in a controlled manner, and the polymer used as an initiator in the photopolymerisation of methyl methacrylate to produce a branched polymer. Attempts to introduce bromine into the carbon skeleton by the copolymerisation of styrene and  $\alpha$  or  $\beta$  bromostyrene were unsuccessful (31). After studying the viscosity of these products in solution, Jones (32) reports that the change in the Huggins constant ( $k'$ ) can be wholly attributed to shear dependency. Since variations in  $k'$  values are often used in detecting chain branching, this information is of vital significance.

A wide range of polymers and monomers can be made to form block copolymers if the polymer is swollen in the second monomer and subject to  $\gamma$  radiation. Mesrobian *et al.* (33) have used this method to graft a surface film of polystyrene onto polytetrafluoroethylene. The film will withstand solvent extraction by benzene for 12 hr. Melville (26) also uses  $\gamma$  radiation, to produce a dispersion of trapped polymer radicals which will continue to grow if a second emulsified monomer is added. The turbidimetric titration method (34, 35) is a rapid and convenient way of detecting block, and graft copolymers. It requires very small quantities of materials, but its quantitative use is suspect (36).

An anionic system is described by Szwarc, Levy & Milcovich (37). Naphthalene<sup>-</sup> Na<sup>+</sup> acts as an initiator for styrene polymerisation at -80°C. in

tetrahydrofuran solution. The negative ended polymer is red, and the colour persists after all the monomer has been consumed. The reaction can be further propagated by adding isoprene; indeed, styrene can be added again to produce a third block (38).

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# SURFACE CHEMISTRY AND CONTACT CATALYSIS<sup>1</sup>

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These areas have remained very active, although progress is steady rather than startling. In the field of electrical properties of substances, the gap between surface chemists and solid state physicists is being rapidly closed or has disappeared. In catalysis, the use of isotopic labelling and concomitant refinement of method proves fruitful; the broadening and deepening of electronic aspects of catalysis continues, although this area is primarily in a data-collecting state.

Among events that have occurred is the first International Congress on Catalysis at Philadelphia in September, and preprints of the proceedings are to appear as Volume IX of *Advances in Catalysis*. A symposium on chemisorption held at Keele, North Staffordshire in July is to appear in book form, while some reports on a symposium on "The Surface Reactions of Gases on Metals," sponsored by La Société de Chimie Physique in Paris, in May, have already appeared in the journal of the society. A meeting of the Deutsche Bunsen-Gesellschaft in Freiburg in May, to be reported in *Zeitschrift für Elektrochemie*, devoted a considerable portion of its time to the subjects of this review. A number of symposia on solid state physics and semiconductors which dealt in part with adsorption and catalysis were held in several countries. This evident vitality and interest is gratifying.

Volume IV of *Catalysis* (P. Emmett, editor) gives extensive coverage of the Fischer-Tropsch and related reactions. Volume VIII of *Advances in Catalysis* contains a masterful review of adsorption phenomena by deBoer.

It is a matter of regret that many excellent papers could not be included in this review, and no attempt has been made at universal coverage.

## SURFACE STUDIES

### PHYSICAL ADSORPTION

*Theoretical and thermodynamic aspects; adsorption isotherms.*—In recent years several papers have indicated that the adsorption of helium at very low temperatures is somewhat unusual. Analysis of the data by the B.E.T. theory gives surface area values two or three times greater than those expected for the adsorbents. Meyer (1) & Steele (2) have independently considered this problem. Both authors conclude that the discrepancy is caused by a deviation from a basic assumption of the B.E.T. theory, that the energy

<sup>1</sup> The survey of literature pertaining to this review was concluded in December, 1956.



of adsorption in the second and subsequent layers is equal to the energy of vaporization of the bulk phase adsorbent. Meyer suggests that the  $v_m$  values of the B.E.T. theory should be interpreted as equal to the volume of gas adsorbed under conditions where  $(\bar{E}_a - E_0) > RT$  ( $\bar{E}_a$  is the differential energy of adsorption, at a concentration  $a$  of adsorbate, and  $E_0$  is the energy of vaporization of the bulk phase). In order for  $v_m$  to assume the usual B.E.T. theory interpretation, as equal to the volume adsorbed in a monolayer, the relation  $2RT < E_1 - E_0 < 8RT$  must be obeyed ( $E_1$  is the adsorption energy in the first layer). Meyer also presents helium adsorption isotherms on gold foil at 2°K., which exhibit some stepwise character. His generalized conclusion that such stepwise isotherms cannot be produced with most gases, even on a homogeneous surface, because of the relatively small difference in heat between adjacent layers, is, of course, incorrect as shown by experimental observation [(3) and references cited therein]. The neglect of lateral interaction between the adsorbed molecules is a contributing factor in this erroneous conclusion. Steele has approached the problem in a similar way, taking into account the differences in adsorption energy between the first, second and subsequent layers. Using a modification of a general isotherm of Dole (4), he obtains satisfactory agreement with experimental data.

A point of practical interest regarding the determination of surface area by the B.E.T. method is given by MacIver & Emmett (5). Benson & Young had obtained a negative value of the coefficient  $C$  for the adsorption of nitrogen on sodium chloride. This is due to the fact that the experimental points were not obtained at sufficiently low pressures, the B.E.T. plot being linear only for  $p/p_0 < 0.1$ . Extrapolation of the linear portion of the curve gives a normal  $C$  value. The limited range of applicability of the B.E.T. theory in this system is attributed to the fact that the adsorbate surface is relatively uniform, exhibiting a tendency towards stepwise nitrogen adsorption.

Further application has been made of the Interpolation Theory to analysis of adsorption data. Honig (6) has shown that the method yields a satisfactory analysis when applied to data for the adsorption of helium on charcoal and neon on glass, at liquid hydrogen temperatures. The application to the adsorption of nitrogen, oxygen and argon on rutile, at 77°K, gave wide divergence of the experimental curves from the theoretical limits, particularly at high coverage [Honig & Reyerson (7)]. The reasons for this are discussed.

"Net" heats of adsorption, defined as the difference between the heat of adsorption of an adsorbate and its bulk latent heat of condensation, are sometimes used in the literature. Graham (8) has discussed the occurrence of negative values of this function when the latent heat is the larger of the two terms and the adsorption occurs without lateral interaction. Using published data for the adsorption of water by graphon, he estimates that an interatomic separation of 12 Å will result in negligible interaction. This separation corresponds to  $\theta/11$  for the first layer, while the experimental value is  $\theta/1500$ . Therefore, in this system the interaction requirement is

easily fulfilled, provided no clusters of adsorbate molecules occur.

Further studies have been made on the thermodynamic properties of adsorbed gases. Pace *et al.* (9) have measured heat capacity and isotherms for the adsorption of krypton on anatase, at 12° to 140° K. In contrast to previous measurements on rutile, a positive value is obtained for the zero point entropy of the system. The values at surface coverages of 0.13 and 0.4 are  $1.1 \pm 1.1$  and  $1.3 \pm 0.3$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>. This is strong evidence that the gas is not in thermodynamic equilibrium with the surface. Calculations indicate that the random order prevailing at 50°K. is retained at the lower temperature investigated.

Heat capacity data between 50° and 75°K. for nitrogen trifluoride adsorbed on anatase show that a phase transition occurs between 4.9 and 5.9 adsorbed layers, indicating the appearance of bulk phase properties [Siebert & Pace (10)]. The difference in the partial molar heat capacities at these two temperatures agrees satisfactorily with the latent heat of fusion of nitrogen trifluoride. No evidence was obtained for a solid phase transition in the adsorbed gas although in the bulk phase this heat of transition is four times greater than the heat of fusion.

Kington and his co-workers have published further on intracrystalline sorption. The thermodynamics of three sorption models have been presented (11), including those for a localized phase and for a mobile phase having either one or two translational degrees of freedom. Experimental isotherms and entropies, for the sorption of argon in chabazite, have been analyzed using the above models (12). The data fit the model for a mobile phase having one degree of translational and two degrees of vibrational freedom, for concentrations, between 0.1 and 0.7 of the saturation value,  $\theta$ . Above  $\theta = 0.7$  this model is no longer applicable; the change is interpreted as caused by "the mutual caging action" of sorbate molecules rather than by mutual interaction between the sorbed molecules. The concept of "mutual caging" would appear to involve such interaction and the reasons for its exclusion are not clear. In a subsequent paper (13) on the interpretation of the heat of sorption of argon in chabazite, interaction terms were introduced. Examination of the crystal structure of chabazite shows that the sites available for sorption are large enough to accommodate two argon atoms at their equilibrium separation of 3.84 Å, but the introduction of a third atom results in a compression of the internuclear distance to 3.41 Å, decreasing the heat of adsorption. Isothermic heats were computed for a random distribution of atoms in groups of two and three throughout the available sites. The theory gives qualitative agreement with experiment, the peak of the isothermic heat curve being of the correct magnitude but shifted to lower concentrations.

An extension of this work, to include diatomic molecules, was made in a study of the sorption of oxygen in chabazite (14).

The study of the growth of crystalline layers of an adsorbate on an adsorbent has been approached by Singleton & Halsey (15) by the measurement of adsorption isotherms. The method has been applied to the formation of

ice layers on surfaces of anatase and silver iodide (16) and shows that three layers of water may be adsorbed on anatase before condensation in bulk crystals is predominant. On silver iodide, however, no trace of the formation of ice layers could be detected by the above technique, and supplementary experiments showed no measurable adsorption of water at  $-45.2^{\circ}\text{C}$ . The conclusion, that the growth of ice layers does not occur on silver iodide under equilibrium conditions, is rather surprising in view of its nucleation properties.

Bonnetain *et al.* (17) have reported further examples of stepwise isotherms obtained for the adsorption of methane at  $-195^{\circ}\text{C}$ . The adsorbents include  $\text{MoO}_3$ ,  $\text{CdBr}_2$ ,  $\text{MnBr}_2$ ,  $\text{NiBr}_2$ ,  $\text{CoI}_2$ , and  $\text{PbI}_2$ . These materials and those previously reported all possess a lamellar type of structure of which graphite is a typical example. The surface of each layer is chemically homogeneous, cationic in character and exposes only one interatomic spacing. This distance is, with the exception of  $\text{MoS}_2$ , within 10 per cent of the carbon-carbon separation in the crystal of methane. The authors suggest that this results in the adsorption of methane in a form close to the crystalline state, allowing substantial lateral interaction, and is a major factor in the production of stepwise (layer by layer) adsorption.

The adsorption of xenon on a nickel film has been studied by Suhrmann (18) who measured the change in the work function and the change in electrical resistance of the film during adsorption. The decrease in work function of 0.7V and the increase of 0.6 per cent in the resistance are explained on the basis of polarization of the xenon which penetrates the film surface and restricts the movement of electrons.

*Experimental techniques.*—Rosenberg (19) has described a convenient system for the measurement of small surface areas, using krypton adsorption at low temperatures. The method has also been extensively studied by Haul (20) who discusses factors involved in the use of this technique, including the value of the krypton cross-sectional area. Values of the krypton vapor pressure at low temperatures are given.

Garbatski & Folman (21) describe the difficult technique of determining multilayer adsorption by electrical capacity measurements. The adsorbent was a pair of parallel glass plates mounted on metal condenser plates. Precise control of the temperature and sensitive capacity measurements are essential. The method was used to study the adsorption of water and of isopropyl alcohol for partial pressures of 0.505 to 0.9976 and 0.2 to 0.993 respectively. Extensive adsorption is reported to a depth of several hundred Ångströms. The results are interpreted using a polarization theory of adsorption developed by Bradley (22).

The application of nuclear magnetic resonance techniques to study adsorbed molecules is reported by Fuschillo & Aston (23) and Mays & Brady (24). Preliminary results for methane on anatase (23) indicate that the adsorbed gas has a very small relaxation time for translation and rotation, at the monolayer coverage. The results are in agreement with thermodynamic

data previously reported by Pace, Heric & Dennis (25) who found the adsorbed molecules to be mobile.

A rapid method of determining the pore volume of a solid has been described by Benesi *et al.* (26). The sample was equilibrated at room temperature with a solution of carbon tetrachloride to which cetane was added to lower the vapour pressure and reduce interparticle condensation. The weight of carbon tetrachloride adsorbed gives data which are as accurate as those obtained by low temperature nitrogen adsorption.

Cranston & Inkley presented a method for obtaining pore size distributions, from nitrogen adsorption isotherms, which is thought to provide information on the shape of the pores (27). Dubinin has made a comparative analysis of sorption methods for the determination of pore structure (28).

#### CHEMISORPTION

Ehrlich has extended his discussion (29) of chemisorption on metals (30). The assumption is made that the initial process leading to the chemisorbed state is physical adsorption of the gas by the surface. An analysis is made for adsorption on a nonuniform surface where the chemisorption may be controlled by the rate of diffusion of physically adsorbed molecules to the chemisorption site, or by the velocity of reaction at the site. The theory is applied to the data of Becker & Hartman for nitrogen adsorbed on tungsten. At low coverage the adsorption is diffusion controlled with reaction occurring at sites of atomic dimensions, tentatively associated with lattice steps on the surface.

A more extensive experimental study of the nitrogen-tungsten system has been initiated using the flash filament technique [Ehrlich *et al.* (31 to 34)]. The existence of several different energy levels of adsorption is shown by allowing adsorption to reach equilibrium at a given temperature and subsequently studying the desorption on flashing the filament to successively higher temperatures. Four adsorbed species are identified after adsorption at 80°K. and characterized by the temperatures at which they are individually desorbed. The  $\gamma$  and  $\delta$  species are observed only at low temperatures and are assumed to involve physical adsorption with a small energy of interaction (34). The heat of adsorption is less than 10 kcal./mole for the  $\gamma$  state (32) which is desorbed at 140° to 250°K. A smaller heat is involved for the  $\delta$  state since it becomes unstable between 100° and 140°K. The preliminary results at 80°K. do not show any transfer from the  $\gamma$  energy level to the chemisorbed states, although the  $\delta$  level appears to pass to the other levels (34). At considerably higher temperatures two further adsorbed species may be desorbed. Between 300° and 650°K. the  $\alpha$  state is removed and at 1400° to 1900°K. the  $\beta$  state desorbs (34). The binding energy of the  $\beta$  state is 85 to 150 kcal./mole. (30, 34), almost certainly corresponding to chemisorption as atoms. The  $\alpha$  state is not appreciably filled until the  $\beta$  state is filled. The evidence suggests that the  $\alpha$  state corresponds to the adsorption of nitrogen molecules on sites generated by the filling of the  $\beta$  state (30). The studies have been extended to the adsorption of carbon monoxide and oxygen on tungsten (33).

In both cases  $\alpha$  and  $\beta$  types of adsorption are noted at high temperatures, and as in the case of nitrogen the  $\alpha$  states are only appreciably filled after completion of the  $\beta$  adsorption.

From these data it does not appear that a definite conclusion can be reached on the existence of a physically adsorbed precursor to the chemisorbed state. As the temperature increases, the equilibrium coverage of the physically adsorbed species becomes too low to detect although this does not necessarily invalidate Ehrlich's postulate (29, 30). A similar situation is discussed by de Boer (35). When a gas is adsorbed endothermically, no surface coverage can be observed but nevertheless it may serve as an intermediate stage in catalysis. He discusses the *ortho-para* hydrogen conversion on sodium chloride, H—D exchange on  $\text{Al}_2\text{O}_3$  and other examples.

Greenhalgh, Slack & Trapnell (36) have studied the adsorption of nitrogen on evaporated metal films of W, Mo, Ta, Nb, Cr, and Fe. On all these metals three types of adsorption are found. Below room temperature the rapid adsorption includes an irreversible, chemisorbed species and a weaker adsorbed species which becomes negligible above room temperature. In addition, a slow sorption process occurs at room temperature. The relation between the adsorbed species described here and the detailed study of the nitrogen-tungsten system by Ehrlich (31) is not clear. It seems that the  $\alpha$  and  $\beta$  states of Ehrlich must both be included in the rapid, irreversible adsorption of the present work, since the maximum desorption temperature is only 373°K. The weak adsorption may include both  $\gamma$  and  $\delta$  states (30). The slow sorption on films finds no parallel in the work on filaments, but this is not surprising since it is relatively minor, for restricted times of adsorption, and perhaps not distinguishable by thermal desorption. Greenhalgh *et al.* (36) compare the extent of the irreversible nitrogen adsorption on each metal to the total surface area measured by low pressure oxygen or hydrogen chemisorption. The adsorption is less than half a monolayer on all metals, the remaining surface being capable of hydrogen chemisorption, but not to a full monolayer. The slow sorption is proportional to the square root of the nitrogen pressure, possibly indicating diffusion into the metal lattice.

*Magnetic and resistance measurements.*—Selwood and co-workers have examined chemisorption on silica supported nickel catalysts by following changes of the specific magnetization using an apparatus of the Faraday type (37) and a modification of a simple method attributable to Weber (38, 39). The latter technique may conveniently be used to observe changes on a catalyst during its operation. The adsorption of hydrogen produces a marked decrease in specific magnetization, interpreted as being produced by electron transfer to the *d*-band levels of the nickel; oxygen, carbon monoxide, and nitrous oxide are shown to increase the specific magnetization by electron transfer in the opposite direction (37, 39). The result obtained for oxygen is not in accord with a similar study by Broeder *et al.* (40). These workers show that chemisorption produces a decrease in magnetization but that local oxidation of the nickel, under the influence of the high heat of chemisorption,

can mask this effect. At room temperature Selwood finds 50 per cent of the hydrogen is very weakly held in a chemisorbed layer and may readily be removed by evacuation (38). A similar observation was also made in a study of the electrical resistance changes by hydrogen adsorption on evaporated films of pure nickel [Singleton (41)]. Selwood *et al.* report anomalous behavior for hydrogen adsorption on very small particles of nickel (37, 39). The magnetization is increased, rather than decreased as on large particles. This behavior is interpreted as a tendency to produce a "nickel hydride" type of bond on particles of near atomic dimension.

Selwood (39) compares the changes in magnetization produced by various gases to the resistance changes observed on thin films of evaporated nickel [Suhrmann & Schulz (42)]. The agreement is surprising since it seems clear that the above results on supported nickel cannot be directly related to pure nickel in that the conditions of outgassing are certainly inadequate to completely desorb hydrogen from a clean nickel surface. It is significant to note that considerable disagreement exists regarding the electrical resistance changes produced by the adsorption of gases on the transition metals. Sachtler & Dorgelo (43, 44) have reported that for nickel the surface is seriously contaminated by evaporation under vacuum conditions of  $10^{-6}$  mm., resulting in slow uptake of hydrogen and a decrease in resistance, as reported by Suhrmann & Schulz (42). In experiments carried out on a cleaner nickel surface, the adsorption was observed to be very rapid and gave an increase in resistance. Singleton (41) also studied the system and described three distinct adsorption processes. An initial, rapid hydrogen uptake at pressures below  $2 \times 10^{-6}$  mm. gave a decrease in resistance, in agreement with Suhrmann (42). At higher pressures of hydrogen, further rapid and reversible adsorption occurred, giving an increase in resistance. This reversibly adsorbed hydrogen is shown to be responsible for the *ortho-para* hydrogen conversion. Finally, a slow sorption of hydrogen giving a resistance increase took place which produced pronounced deactivation of the catalyst activity towards the *ortho-para* hydrogen conversion. The vacuum conditions used in this work are intermediate between the extremes described by Sachtler (44), but the rapidity of the observed adsorption argues against extensive contamination. Considering the complexity of the adsorption process noted as the equilibrium pressures are increased, it seems difficult to assess the overall status of the nickel-hydrogen system in the absence of further experimental studies.

A study of hydrogen adsorption on platinum by Mignolet (45) gives rise to results in complete contradiction of previous work, the discrepancy again being attributed to the use of contaminated metal surfaces. Measurements of the contact potential were made on films of evaporated platinum, showing the presence of two types of adsorption. At low coverage the chemisorption of atoms occurred, giving a negative contact potential. At higher coverage, molecular adsorption with an approximate heat of 15 kcal./mole, resulted in a positive contact potential.



*Rates of adsorption.*—Wagener describes a method of measuring rates of chemisorption at very low pressures (46). Values of 5 l./sec.cm.<sup>2</sup> are obtained for the adsorption of carbon monoxide and carbon dioxide on barium, strontium, and nickel. The activation energy of the adsorption on barium is less than 0.2 kcal./mole. The method is also valuable at much slower rates of adsorption.

The absolute rate theory has been used to derive the so-called Elovich equation [Higuchi, Ree & Eyring (47)]. It is suggested that the name "Becker-Zeldovich" is more appropriate for this type of expression. It is assumed that, for the adsorption of alkali atoms on a tungsten surface, a Helmholtz double layer is formed. The equation

$$-d\theta/dt = a\theta \exp(b\theta)$$

is derived for the rate of desorption, where  $a$  is the frequency of transformation of an adion to an adatom on the bare surface and  $b$  is the ratio of the decrease of activation energy, for desorption at  $\theta = 1$ , to the mean kinetic energy of the adion. The adsorption is similarly expressed as

$$d\theta/dt = a(1 - \theta) \exp(-b\theta)$$

The theory gives satisfactory values for the polarization of the adion and for the distance of the adsorbed layer from the surface. A further discussion of the equation is given by Meller (48) while Sarmousakio & Low (49) give a convenient and precise numerical method of evaluating the equation.

*Field ion and field emission microscopy.*—The elegant methods of field emission and field ion microscopy have, as yet, been little exploited in the investigation of the adsorption of gases. The techniques and results of these methods have been reviewed (50, 51). Several notable advances have been reported. Müller has developed the field ion microscope to obtain a resolution of the order of 1.5 Å using a 1000 Å diameter tungsten emitter (52, 53, 54). Emission patterns are reproduced showing the individual atoms of the tungsten surface.

It is important to observe that some of the virtues of these techniques are grave disadvantages in the study of adsorbed gases, which when subjected to the enormous electrical fields are not in the normal equilibrium condition on the surface. This defect is overcome to a large extent by a modified technique of Dyke and co-workers (55, 56) in which the electrical field is applied in pulses of the order of a microsecond at a rate of 30 to 1000 pulses per second. Thus, the total time during which the field is applied is very small. Using this method emitters such as iron and nickel may readily be studied.

Wortman, Gomer & Lundy (57) have continued work on the surface diffusion of oxygen and hydrogen over tungsten. When a monolayer is deposited on a (011) oriented tungsten tip, boundary migration sets in at 205°K. for hydrogen and 500°K. for oxygen. The mode of spreading is described. The activation energies of ~9 kcal./mole and ~19 kcal./mole, for hydrogen and oxygen respectively, are considerably below those obtained at lower coverages (16 and 30 kcal./mole), which correspond to escape from the unfilled



high energy sites. The figure for oxygen on tungsten, at high coverage is comparable to a value of  $\sim 16$  kcal./mole obtained by Müller (58).

*Adsorption on semiconductors.*—Gray & Darby discuss the relations between the defect nature of a solid and adsorption kinetics, with detailed consideration of oxides (59). The nickel oxide system has been studied (60) using measurements of the changes of semiconductivity produced during adsorption. The extreme complexity of the system is illustrated and a correlation is made with previous work. Several papers, such as that of Harada & Minden (61), which describe the effect of gas adsorption on electrical conductivity and related properties of semiconductors, have been omitted because of lack of space.

Jennings & Stone (62) have studied the kinetics of chemisorption of oxygen on cuprous oxide. The oxide is prepared by controlled oxidation as a surface which is readily regenerated and reproducible. The adsorption is largely irreversible, giving several monolayers. The energy of activation in the first layer is 7 kcal./mole and is higher for the subsequent layers. Oxygen uptake after the monolayer occurs by a mechanism involving migration of cuprous ions to the surface.

The flash filament technique is used in a study of adsorption on silicon by Law & Francois (63). The adsorbent is cut from single crystal silicon. No adsorption of argon, nitrogen, or carbon dioxide is detected, while hydrogen and carbon monoxide are reversibly chemisorbed. Oxygen reacts rapidly to give approximately five layers, the process being regarded as oxidation after the chemisorption of a monolayer. Water is also irreversibly adsorbed.

#### PREPARATION OF SURFACES

The problem of obtaining a well defined surface for adsorption and catalytic studies is one of great difficulty. A general method of achieving a uniform surface for physical adsorption is proposed by Steele & Aston (64). A fraction of a monolayer of a rare gas is preadsorbed on the adsorbent under study. As an example, the heat of adsorption of helium was determined on a titanium dioxide surface covered with one half a monolayer of argon and compared with that on the bare adsorbent surface. The heat of adsorption on the argon-titanium dioxide surface was almost constant at all helium coverages, while that on the bare surfaces was high and fell off rapidly with coverage. The results indicate that the preadsorbed argon preferentially occupies the higher energy sites, markedly reducing the surface heterogeneity.

The problem of obtaining a clean surface for chemisorption is far greater. In a few cases, such as tungsten (31) and silicon (63), the surface may be obtained by heating to very high temperatures ( $> 1000^\circ\text{C}.$ ) under excellent vacuum conditions ( $< 10^{-8}$  mm.). These surfaces have relatively small surface area and require extreme care to maintain in a clean state. The evaporation of films of large surface area, after the method of Beeck, has been extensively used, but even this method has been criticized (31).

Farnsworth *et al.* (65, 66) have shown the rigorous treatment necessary

to produce a clean metal surface. Nickel and platinum were subjected in succession to high temperature outgassing in a vacuum of the order of  $10^{-10}$  mm., bombardment by argon ions and an annealing at  $500^{\circ}\text{C}$ . The final process removed argon ions and reduced the bombardment-induced imperfections on the surface. The cleanliness of the surface was checked by diffraction of a low energy electron beam. To clean a nickel crystal (66) the cycle was repeated many times to a total treatment of 400 hr. outgassing at  $800^{\circ}\text{C}$ ., 5 hr. at  $1100^{\circ}\text{C}$ . and 3 hr. argon ion bombardment. This extensive treatment was found necessary because of the diffusion of a bulk impurity, possibly carbon, to the crystal surface.

Lecke has shown that ion bombardment may result in the penetration of ions to a depth of several atomic layers (67). The ions are removed by a short outgassing treatment at  $500^{\circ}$  to  $600^{\circ}\text{C}$ . Law & Garrett quote results to suggest that ion bombardment is inadequate to clean a germanium surface (68). They show that oxygen, chemisorbed on the surface following the cleaning process, can be readily removed by heating at  $300^{\circ}$  to  $400^{\circ}\text{C}$ . for 2 min. in a vacuum, and suggest that an oxygen monolayer is present on the surface at all times.

#### MISCELLANEOUS

The difficulty of obtaining measurements of the heat of adsorption of oxygen and the problem of localized heating on nickel is examined by Dell, Klemperer & Stone (69). Parravano *et al.* (70, 71) have studied the heat of adsorption of oxygen on nickel, platinum, silver, palladium, and palladium-silver alloys. The data were obtained from the decomposition equilibria of water vapor on these metals. The value obtained on nickel is much lower than those of Dell *et al.* (69).

Morrison & Patterson have studied the heat capacity of small particles of sodium chloride over a temperature range of  $12^{\circ}$  to  $270^{\circ}\text{K}$ . (72). The experimental measurement of the surface energy of sodium chloride has been repeated by Benson *et al.* (73). A value of the surface enthalpy of  $276 \text{ ergs cm.}^{-2}$  is reported, appreciably less than an earlier determination of  $305 \text{ ergs cm.}^{-2}$ . However, the new value is still considerably greater than that predicted theoretically. Brunauer, Kantro & Weise have obtained the surface enthalpy of calcium oxide and hydroxide (74), and of amorphous silica and hydrous amorphous silica (75).

#### CATALYTIC REACTION

##### INFRARED SPECTRAL MEASUREMENTS

The infrared adsorption spectra of adsorbed molecules have been enhanced in their importance for chemisorption and catalytic phenomena by extension of techniques to transition metal surfaces by Eischens, Francis & Pliskin, in a study of carbon monoxide adsorption (76). The spectra of the adsorbed species were obtained as a function of surface coverage. On nickel

and palladium, the spectra indicate several different types of sites and suggest two types of bridged carbon monoxide adsorption, with a less strongly held species bonded to a single metal atom. On platinum only single bond adsorption took place. This agrees with the recent study of carbon monoxide on platinum films made by Lanyon & Trapnell (77), but not with their findings on palladium, nor with those of Baker & Rideal on nickel films at 20°C. (78). However, only general agreement between these spectral results and adsorption studies on clean films can be expected, in view of the preparation and treatment of the supported metal wafers.

The spectra of the chemisorbed species from carbon dioxide on nickel oxide ("bicarbonate" ion) and on supported nickel (carboxyl ion), as well as the postulated intermediate,  $\text{Ni}-\text{O}-\text{C}\equiv\text{O}$ , produced upon oxidation of carbon monoxide over a nickel-nickel oxide catalyst, have been reported [Eischens & Pliskin (79)]. For physical adsorption of  $\text{CO}_2$  on Cab-O-sil support ( $\theta = 0.01$ ), a single band at  $4.26\mu$  was obtained in place of the doublet in this region, indicating that the adsorbed molecules do not rotate freely.

Pliskin & Eischens (80) examined the spectra of ethylene, propylene, and acetylene on nickel. As with carbon monoxide, most data were obtained on a catalyst pumped free of hydrogen at room temperature, hence hydrogen covered. As a consequence, the absence of a  $\text{C}=\text{C}$  stretching band for chemisorbed ethylene and propylene, and the presence of a  $\text{CH}_2$  deformation band for ethylene, may not be conclusive evidence in favor of associative adsorption, although it is true that subsequent introduction of hydrogen produced new bands, identified as belonging to the half-hydrogenated ethyl intermediate. If hydrogen was pumped off at 350°C., admission of ethylene in small amounts gave rise to chemisorbed species containing no  $\text{C}=\text{C}$  double bonds. Since Jenkins & Rideal (81) have shown that initial chemisorption of ethylene on nickel films does not give rise to  $\text{CH}_2\text{CH}_3$ , it appears reasonable, as suggested by the authors, that the adsorbed species may be  $\text{HC}-\text{CH}$ , rather than the more conventional,  $\text{HC}=\text{CH}$ . Calculations of the heats of chemisorption of ethylene on nickel for various models have yielded values markedly less than the experimental values at low surface coverage (82); use of the  $\text{HC}-\text{CH}$  model would tend to decrease the discrepancy.

Upon chemisorption of acetylene,  $\text{CH}_2$  and  $\text{CH}_3$  deformation bands appear (80). An attempt was made to rule out reaction due to residual surface hydrogen by use of a deuterated surface, whereupon  $\text{CH}_2$  and  $\text{CH}_3$  bands still appeared. Pliskin & Eischens conclude that this indicates that self-hydrogenation occurs. Although these bands could arise after initial exchange of acetylene with surface deuterium, their conclusion appears quite probably correct.

Improvements and extensions of the technique for preparing suitable adsorbent materials may be expected, as well as possible application of fast

scanning techniques, and it appears that spectroscopic studies, so signally advanced by the investigations cited here, provide a powerful tool for studying the nature of both adsorbate, adsorbent and catalytic reaction.

#### APPLICATION OF ISOTOPES; MECHANISMS

*Ethylene hydrogenation, exchange, and isomerization.*—This subject continues to invite intensive study with emphasis on elucidation of the problem by use of hydrogen isotopes. Flanagan & Rabinovitch have introduced a new and useful concomitant reaction to hydrogenation and exchange, namely *cis-trans* isomerization. They studied the time course of the equilibration reaction of *trans*-ethylene- $d_2$ , and of mixtures of light and heavy ethylene, on nickel wire (83), as well as the kinetics of isomerization and exchange of *trans*-ethylene- $d_2$  on nickel wire in the absence of hydrogen (84). The isomerization and exchange reactions exhibit identical kinetics over a considerable temperature region and must involve the same mechanism. A small difference in activation energies between these reactions is explained as an isotope effect. The results rule out conventional Farkas and Beecck mechanisms as the sole reaction process and indicate that dissociative adsorption processes are followed by formation of an intermediate ethyl radical, whether by an associative or Rideal mechanism. Exchange products are produced in a step-wise manner and the results show both that reversible adsorption of ethylene on a fully-covered nickel surface takes place, and that the surface equilibrates with the gas phase at the temperature employed (above  $-80^\circ$  C.). In the presence of deuterium (85), *cis-trans* isomerization and exchange are much faster than hydrogenation below  $100^\circ$ C. for a 1:1 ethylene- $d_2$ -hydrogen mixture.

Kemball (86) has presented valuable data on the interaction of 1:3 mixtures of ethylene and deuterium on nickel, iron, rhodium, and tungsten films at  $-100^\circ$ C. A general model is given for calculating the distribution of deuterated ethylene and ethane products, whose time course of production was also determined experimentally. The results show that deuterated ethanes arise from ethylene exchange processes. Very little hydrogen is returned to the gas phase. It is suggested that the difference from the results of Wilson *et al.* (87), who observed no deuterioethylenes with a 1:10 ethylene-deuterium mixture on supported nickel, may result from the different catalysts employed. However, Flanagan & Rabinovitch (85) working on nickel wire and nickel-kieselguhr with a 1:1 mixture found large amounts of ethylene exchange, and the relative proportions of the reactants is probably a significant factor in determining the relative amounts of products, particularly if the dependence of ethylene exchange upon deuterium pressure is not to the first, but to the half power (86, 88). The value of 6 to 7 kcal./mole for the activation energy for exchange found by Kemball is checked by that of other workers for nickel wire around room temperature (85), and is, of course, markedly less than the value obtained when ethylene exchange is followed by hydrogen return to the gas phase.

A difference, which could be reconciled by the different experimental conditions employed (85), arises between the results of Kemball and those of Flanagan & Rabinovitch (85) and Jenkins & Rideal (81). The experiments of the latter lead to the conclusion that a Rideal mechanism applies for exchange. This conclusion is compatible with the results of Flanagan & Rabinovitch who found only single step exchange initially, but not with those of Kemball whose initial products included multiply exchanged ethylenes.

The criticism by the latter of the "three atom" mechanism of Couper & Eley (89) for hydrogen-deuterium exchange and *ortho-para* hydrogen conversion, based on the demonstration (81) that chemisorbed hydrogen exists on an ethylene-covered nickel surface, depends on the proposition that these reactions are virtually completely inhibited on an ethylene covered surface. Although Kemball may be correct, this latter proposition may be stronger than the experimental data which supports it (90) and a thorough experimental re-examination would be in order. The results of Schissler, Thompson & Turkevich should be compared (91).

The addition of deuterium to ethylene has been studied by Bond (92) over a variety of platinum catalysts to provide a maximum of internal consistency in a study of the influence of catalyst variables on the kinetics and products of reaction. The results indicate that the same mechanisms operate for all catalysts but with relative rates that depend on the catalyst preparation. The data obtained refer primarily to the structure of the ethane- $d_x$  products which appear to decrease logarithmically as  $x$  increased from 2 to 6. The proposed model given in explanation conforms with the general model of Kemball (86).

Keii (93) has expanded his fine structure model for the distribution of deuteroparaffins resulting from catalytic deuteration of ethylene and other olefins. Kemball's model (86) is closely related to that of Keii.

*Other exchange and hydrogenation reactions.*—The isotopic exchange reaction between deuterium, tritiated hydrogen and light water has been studied at 25°C. by Hannerz (94) on platinum foil, using radiotracer and mass spectrometric techniques. The data are reconciled by a mechanism involving dissociative chemisorption of both hydrogen and water on the surface. Miyahara (95) has applied Keii's fine structure model to data on ethane-deuterium exchange on various metal films.

A finding of potential synthetic value, apart from its intrinsic interest, has been made by Burwell & Littlewood (96). Chromium oxide gel dehydrated above 400°C. acquires hydrogenation activity. With deuterium at low temperatures, -78° to 40°C. depending on the substrate, ethylene, 1-butene, cyclopentene, and 1-hexene give dideuteroalkanes almost exclusively. At higher temperatures the deuterium distribution pattern of the products broadens and resembles those obtained with transition metal catalysts. The results of Komarewsky & Miller (97) should be compared. Burwell & Littlewood showed that dehydrated chromium oxide gel gives single deuterium atom exchange of hexane for deuterium-hexane mixtures at 200°C.

At higher temperature, multiply exchanged hexanes were found which, it is suggested, do not arise from multiple exchange as such, but by deuteration of hexenes resulting from dehydrogenation.

The exchange products resulting from deuterium addition to cyclopropane on rhodium, palladium, iridium, and platinum pumice catalysts have been shown by Bond & Addy (98) to be similar to the distribution obtained at longer times and higher temperatures in the exchange of propane and deuterium; propane- $d_7$  and propane- $d_3$  predominate. The suggestion that the primary reaction for cyclopropane is adsorbed *n*-propyl radical formation while that for propane is *iso*-propyl radical formation, and that these radicals are in equilibrium on the surface, is supported by experiments with *n*-propyl chloride and *sec*-propyl chloride and deuterium on palladium; the exchanged propane products were closely similar. The activation energies for propane exchange were  $\sim 17$  kcal./mole on each catalyst. The results reveal only minor differences between the catalysts employed and seem not very useful in elucidating the geometric and electronic factors of the catalysts.

The value of deuterium labelling coupled with careful and detailed mass spectrometry is again illustrated by work of Anderson & Kemball (99) on the fine structure of benzene exchange and hydrogenation with deuterium, on palladium and platinum films primarily, but with data also on tungsten, iron, nickel, and silver films. Unlike ethylene hydrogenation and exchange, these processes for benzene appear to occur by quite separate mechanisms, as revealed by different kinetics, relative rate ratios and variation with the catalyst, and inhibition only of the exchange by cyclohexane product. Addition of a molecule of deuterium (or a pair of atoms) to an associatively adsorbed benzene species is suggested as the mechanism of deuteration, and accounts for the minimum deuterium content of the product corresponding to cyclohexane- $d_4$ . Amano & Parravano (100) studied the hydrogenation of benzene on alumina-supported ruthenium, rhodium, palladium, and platinum catalysts, and found the same rate dependence on reactant concentrations on ruthenium that Anderson & Kemball found on palladium (first order in hydrogen and zero order in benzene). Their interpretation of this rate law assumes that the slow step is hydrogen adsorption followed by reaction between gas phase benzene and adsorbed hydrogen. The relative activity of palladium was very low in this work and no activation energy is recorded, while Anderson & Kemball found the activation energy on palladium to be the same (9 kcal.) as on platinum, and 3 kcal. less than the value for platinum of Amano & Parravano, who proposed that the reaction of palladium involves the hydride. No evident relation exists between activity and *d*-bond character of the metal films as opposed to the apparent relation found for relative activity of ruthenium, rhodium and platinum on alumina.

On the basis that benzene- $d_1$  is the principal initial exchange product, the adsorbed phenyl radical is proposed by Anderson & Kemball as the intermediate species for this process; while multiple exchange is thought to proceed via a phenylene biradical.



*Other reactions.*—Pines & Shaw (101) used  $C^{14}$  labelling to determine whether the hydroisomerization of a model compound, ethylcyclohexane, proceeds by side chain rearrangement or through a carbonium ion mechanism. With ethylcyclohexane- $\alpha$ - $C^{14}$  over nickel on silica-alumina, most of the  $C^{14}$  activity of the products is in the ring, and it is concluded that a carbonium ion produced resides for a relatively long time on the catalyst with successive ring contractions and expansions to permit virtually equilibrium scrambling of carbon atoms.

The use of optical activity is probably an under-worked diagnostic tool in catalytic mechanisms. Bonner & Zderic (102) have invoked the virtuosity of this method in the study of exchange of (+)-2-phenyl propionamide on deuterated Raney nickel in deuterioethanol. The amount of exchange of ring hydrogen,  $\alpha$ -methyl hydrogen and of  $\alpha$ -hydrogen greatly exceeded the extent of racemization and demonstrates the stereospecificity of the exchange process, although the existence or necessity of a postulated carbonium-ion intermediate is not as apparent.

*Cracking of hydrocarbons.*—Detailed measurements of the water content of variously treated silica-alumina cracking catalysts and their exchange with  $D_2O$  vapor have been made by Haldeman & Emmett (103). Their data and conclusions support the increasing evidence that the Lewis acid coordination model of the catalyst structure is the predominating one, although the existence of a fraction of Brönsted acid sites is not precluded. The relation with actual catalytic activity is considered in another paper in which extensive measurements of hydrogen exchange between isobutane and a number of deuterated silica-alumina catalysts are presented (104). The rate of hydrogen exchange may be taken as indicative of the efficiency of these catalysts for cracking and isomerization reactions [Hindin, Mills & Oblad (105)]. The data of Haldeman & Emmett establish and confirm (105) facts concerning the low reaction rates on catalysts containing very small percentages of water ( $D_2O$ ). These authors attribute the efficacy of small amounts of water to the formation of Brönsted sites as a requirement for chemisorption of isobutane, as opposed to a mechanism involving transfer of a hydride ion from saturated hydrocarbon to a Lewis acid site, and roughly relate the total amount of chemisorption on a particular catalyst to the estimated amount of added water that can be going to form Brönsted sites from Lewis sites. Evidence for diffusion of a deuterium species on the catalyst is derived from the remarkable amount of exchange that occurs with each chemisorbed isobutane molecule.

Danforth (106) has amplified earlier work and presented a consistent picture of the structure and function of silica-alumina catalysts, based on a study of the reaction between aluminum hydroxide and various alkyl silanols, which complements some of Haldeman & Emmett's findings and otherwise extends and ramifies the interpretation of the catalyst action. The active structure of the catalyst is pictured as a double chain of  $>Al-OH$  sites at each edge of a ribbon, the sides of the ribbon exposing silica tetrahedra. It



is proposed that the Lewis acid sites are entirely responsible for the activity and that, following earlier suggestions, water functions as a cocatalyst on dual active sites, with rapid migration of water along the active edge of the ribbon. An explanation of exchange phenomena is offered. In the present interpretation, the movement of the cocatalyst from site to site may function to displace the hydrocarbon from the catalyst.

#### CATALYSIS, ELECTRON TRANSFER AND THE SOLID STATE

Detailed correlation of the catalytic activity of metal and semiconductor catalysts with the properties of metallic and defect solids have not proven as simple or as evident in general as the case for chemisorption studies with simple molecules, or even for simple decomposition reactions. This circumstance hinges in part on the deficiencies of the theoretical approach, but also depends on the complexity of the phenomena, on the fact that the mechanism of the reaction concerned is usually not unequivocally known, not to mention the experimental facts themselves, and, finally, on the paucity of a wide variety of data. Useful information, largely qualitative in its correlation, continues to be gained; emphasis is still placed experimentally on conductivity measurements as the most easily accessible symptom of catalyst condition. Several excellent reviews and developments of the subject have appeared recently in a book dealing mainly with this subject (107).

*Oxides.*—Dowden, Mackenzie & Trapnell (108) have pointed to a relation to be expected in some cases between electronic configuration factors in catalysis by both metals and oxides, which they believe has been overlooked due to the success of the correlation of oxide catalyst activity with the semiconductive property in certain well known, but special cases (oxide ion formation), such as nitrous oxide decomposition and carbon monoxide oxidation. The view is taken, in a study of hydrogen-deuterium exchange on transition metal oxides, that these oxides are ionic and that the metal ion configuration (cf. *d*-band configuration for metals) is an important factor in determining catalytic activity, although apparent exceptions occur. The relative activity for hydrogen-deuterium exchange of thirteen oxides of the first transition series and neighboring elements is shown to be rationalized by the postulate that a small number of unpaired *d*-electrons in the ion is conducive to high activity, which accounts also for the double maximum in activity observed along the series of oxides. Such electronic configurations lead to weak but rapid hydrogen chemisorption, and reaction according to the Bonhoeffer-Farkas mechanism.

Heckelsberg *et al.* (109) studied hydrogen-deuterium exchange from  $-10^{\circ}$  to  $320^{\circ}\text{C.}$  on zinc oxide, variously treated with hydrogen, oxygen, alumina, or lithia, and they coupled rate with conductivity measurements at  $200^{\circ}$  to  $550^{\circ}\text{C.}$  The results in general confirm earlier conclusions and findings concerning this system [Parravano & Boudart (107)]. However, some of the findings, for example, constancy of activation energy over the temperature range, do not accord with earlier work, and internal discrepancies

also exist which demand *ad hoc* rationalization. Nonetheless, the phenomena are generally correlated with the defect structure of *n*-type zinc oxide. Detailed connection of these factors with the exact mechanism of the exchange is less clearly evident even for this simple reaction, and only some of the discussion during the past year or two will be briefly mentioned. Hauffe (107), in an exposition of the barrier layer theory, has proposed as the basis of experimental observations that the slow step in the reaction involves the rate of transfer of an electron to a  $H^+$  ion during the desorption process. Issue has been taken with this point of view by Garner (110), and Stone (111) has postulated hydrogen chemisorption as the rate determining step to rationalize such data. For the chemisorption, the nature of the effective adsorption process has been variously stated (108, 110).

Schwab and his school have broken more new ground in the study of photocatalysis on oxide and other surfaces, of which a summary has been given (112). Electron "acceptor" type reactions on *n*-semiconductors, or of "donor" type reactions on *p*-conductors, which do not proceed in the absence of light will do so upon suitable illumination. The decomposition of hydrogen peroxide on zinc oxide into oxygen and water, and the back reaction, are examples of this phenomenon. Zinc sulfide is similarly active. Introduction of electron traps inhibits the light reaction as expected. Other examples are given of both donor and acceptor reactions on oxides and on *n*- and *p*-doped germanium. The results confirm and support the conclusions heretofore derived from thermal studies.

Schwab & Hartmann (113) studied ozone decomposition on some oxides and hydroxides of the main groups of the periodic table. The reaction depends on the Lewis base behavior of the catalyst. A comparison with nitrous oxide behavior is made. The relative efficiencies of several metals and their oxides in various oxidation states was determined (114). Catalytic efficiency increased with magnitude of metal ion valence. An explanation involving a type of polarization chemisorption is advanced.

Clark & Berets (115) have obtained excellent information regarding the properties of *n*-type vanadium pentoxide powder and films as oxidation catalysts. In addition to conductivity determinations, they made thermoelectric emf. measurements and determined the value of the Fermi level over a range of temperatures and conditions, and found the bulk and surface Tammann temperatures. Measurements were made both in the presence of oxygen and of air (oxygen)-hydrocarbon (ethylene, *o*-xylene) atmospheres. The data are interpreted in terms of the barrier layer theory and comparison of results in the presence and absence of hydrocarbon point up the desirability of employing conditions closely related to actual operating conditions in attempts to relate catalyst properties to activity.

Information concerning the possible role of electron transfer in the cracking of paraffins has been obtained by Franklin & Nicholson (116). For *n*-paraffins, a decline in activation energy with increasing molecular weight is related to a concomitant decline in ionization potential of the substrate

molecule. This supports the view that ionization of the substrate is rate-determining, and is consistent with the picture that the catalysts function as Lewis acids.

*Metals.*—Ethylene hydrogenation has been studied by Cunningham & Gwathmey (117) on the {100}, {111}, {110}, and {321} faces of nickel single crystals at temperatures above 50°C. No roughening or development of the surface occurred during reaction. The {321} face was the most active for hydrogenation while the (100) face was the least active. Specificity of carbon formation by pure ethylene at 450°C. also was found, although no correlation appears between the hydrogenation and decomposition reactions. Geometric factors were ruled out as definitive in determining activity, but the experiments reveal that the part played by these, by electronic factors and by surface imperfections are still not clear.

Suhrmann & Wedler (118) have used the variation of resistance of nickel films as a diagnostic test of mechanism for the decomposition of formic acid at room temperature. They employ the following basis. Upon chemisorption, the possible products, hydrogen and carbon dioxide, raise the conductivity of nickel films (but see discussion under Chemisorption), as does formic acid, electron transfer to the metal taking place. The other possible products, water and carbon monoxide, raise and lower the conductivity, respectively, upon chemisorption, the latter exhibiting a relatively larger effect. When formic acid at  $10^{-6}$  mm. is placed on the film, the initial increase in conductivity is followed by a decrease which is taken to represent carbon monoxide production. Suhrmann & Wedler reconcile this mode of decomposition at room temperature with the production of carbon dioxide and hydrogen found by other investigators at higher temperatures as being due to secondary occurrence of reaction of water with carbon monoxide at high temperatures which greatly favors carbon dioxide and hydrogen. In general, however, the proportions of products that arise cannot be so simply explained or deduced. Walton & Verhoek (119, and references quoted therein), with randomly oriented nickel films in the region 125° to 190°C., find simultaneous dehydrogenation and dehydration reactions, of initial zero order, in the ratio of 3:1 and characterized by a single activation energy value (15.8 kcal.). They note a slight tendency toward dehydrogenation at lower temperatures. Earlier workers (46) have found both carbon dioxide and carbon monoxide at 250°C., while no carbon monoxide was produced at 200°; however, this work does not refer to clean films. Rienacker & Hansen (120) have described conductivity measurements on nickel films upon chemisorption of various gases which are at variance with those of Suhrmann. (However, their technique may expose the films to air.) From their conductivity measurements and results on the formic acid decomposition on nickel films (121) studied in a range around 200°C., where they found as products hydrogen and carbon dioxide and an activation energy of 25 kcal., Rienacker & Hansen conclude that in their experiments the initial step involves electron transfer from the

metal to the substrate, in contrast to the mechanism of Schwab. The status of this reaction can hardly be described as satisfactory.

Pickup & Trapnell (122) have remarked on a relation between the efficiencies of metal surface for hydrogen atom recombination and their *d*-band character, and have suggested explanations for other features of the data.

The *p*-hydrogen exchange has been studied by Rienacker & Vormum (123) on nickel-copper and palladium-copper alloy strips over a range of compositions. The data complement the classical experiments of Couper & Eley on the nature and importance of the *d*-band electron configuration of transition metal catalysts.

Selwood has reviewed the subject of magnetic factors in catalysis (124), including the recently described method (38, 39) of continuous measurement of the *d*-band electron density of a functioning catalyst.

*Catalysis by strained and damaged surfaces.*—Several investigations have been aimed at the examination of the activity of strained and damaged surfaces. Farnsworth & Woodcock (65) have studied the activity for ethylene hydrogenation and hydrogen-deuterium exchange of nickel and platinum surfaces outgassed at high temperatures (800 to 1300°C.) and low pressures; this procedure alone does not yield clean surfaces (see Preparation of Surfaces). Catalytic activity for hydrogenation is enhanced by positive ion bombardment with argon; the activity may be greatly reduced or destroyed by annealing briefly at 500 to 700°C. The high activity following bombardment is presumably due to defects created at the (cleaner) surface of the crystal lattice which are largely removed by annealing.

The hydrogen-deuterium exchange rate on nickel is relatively unaffected by annealing of a bombarded surface and the rate determining steps for this reaction and ethylene hydrogenation evidently differ in their dependence on surface state.

Weller & Hindin (125) investigated the induction of catalytic activity in gamma-alumina by severe dehydration at high temperatures (450 to 650°C.) Decline of water content from 2.3 to 0.4 per cent, with no concomitant change in crystal structure, converts alumina from an acid catalyst to a hydrogenation catalyst. Upon dehydration, the activity increased sixtyfold for ethylene hydrogenation and seventeenfold for hydrogen-deuterium exchange under specified conditions. Small amounts of water (0.15 per cent) act as a poison. Isotheric heats of adsorption of water decline from 100 kcal./mole at "low" coverage to 10 kcal./mole at "high" coverage. The authors propose that both the hydrogenation activity and high heats of adsorption are associated with highly strained sites arising upon dehydration and removal of surface hydroxyl ions.

#### MISCELLANEOUS

The decomposition of ammonia on germanium films, studied by Tamaru

(126) at a single temperature (278°C.), is indicated to proceed by dissociative adsorption of ammonia. The slow step is desorption of hydrogen, but interestingly enough the rate is slower than the similar step in germane decomposition because, it is suggested, the desorption is from next nearest sites and not nearest sites as for germane. This circumstance could offer a valuable insight into the desorption process for hydrogen on this surface.

A novel finding was made by Moss & Kemball (127) in the system cyclohexyl amine-hydrogen over a platinum film at 134°C. The primary product was not the expected cyclohexane but rather benzene. After consumption of most of the cyclohexyl amine occurs, benzene hydrogenation to cyclohexane begins. The mode of decomposition as well as inhibition of benzene hydrogenation are interesting and ramifications may be awaited.

Benesi (128) has extended earlier work of Tamele and used adsorption of Hammett indicators of varying pK to measure and map the Brönsted acid strengths of a variety of catalyst surfaces, including cracking catalysts, and their variation by suitable treatment. The practical utility of this very simple method, as extended, is noted.

Several formulations of kinetic problems in terms of absolute rate theory may be noted. Foss (129) has developed a relation between observed energy of activation and heat of adsorption for unimolecular reaction of order intermediate between zero and first; homogeneous surface was assumed and the problem was explored for two alternative relationships between heat of adsorption and surface coverage. Application was made to the decomposition of ammonia on tungsten, for which it was concluded that experimental reports in the literature actually refer to the intermediate order region and not to the zero order region, as claimed. It has been pointed out by Robertson (130) that the experimental results obtained by him and his co-workers on the dehydrogenation of ethane and propane on a platinum filament, (131) as well as on formic acid dehydrogenation on copper crystals, are not consistent with theoretical rate equations which assume an immobile transition state. The same fact was noted for other earlier work. Better agreement is obtained by use of the Eyring equation in which the transition state is treated as a two-dimensional gas, although even this predicted rate is too small in some cases and for these a postulate of "supermobility" in the transition state is tentatively made. This supermobility, not of the "three-dimensional gas" type described several years ago by Kemball (132), is assumed to involve induced catalyst atom mobility.

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# ELECTRODE PROCESSES<sup>1</sup>

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Louisiana*

This review deals with the kinetics of electrode processes for the two-year period since the last review in this series (1). Earlier work is discussed whenever necessary. The coverage is not comprehensive and some topics are omitted, notably the anodic formation of insoluble films. General reference is made to recent books (2 to 7), important collections of papers (8, 9), reviews (10, 11, 12), a detailed nomenclature of electrochemical terms (13), and comments on this nomenclature (14).

Three general problems of kinetics served as a guide in the organization of material: (a) definition of kinetic parameters, (b) their determination, and (c) interpretation and application to the elucidation of mechanisms. Adsorption effects are treated lastly.

Electrochemical kinetic parameters are defined from current-potential relationships whose fundamental form was derived by Butler, Audubert, and, more correctly, by Erdey-Gruz and Volmer some thirty years ago. [For details see Vetter (15).] An electrode process with a single rate determining step that involves the same number of electrons as the complete electrode reaction can be characterized by the following exchange current density [see Gerischer (16) and Berzins & Delahay (17) for this particular form of the exchange current],

$$i_0 = nFk_s C_{Ox}^{(1-\alpha)} C_{Red}^{\alpha}, \quad 1.$$

where  $n$  is the number of electrons for the electrode reaction;  $F$  the Faraday;  $C_{Ox}$  and  $C_{Red}$  the concentrations of reducible and oxidizable substances, respectively, in the bulk of the solution;  $\alpha$  the transfer coefficient for the cathodic process;<sup>2</sup> and  $k_s$  the rate constant at the formal potential. In addition to  $i_0$ ,  $\alpha$  is characteristic of the electrode process under given conditions. The rate constant  $k_s$  can be used as an alternative to  $i_0$ . Values of  $i_0$  are generally quoted for unit concentration of reactants (in moles per cm.<sup>3</sup>).

In many electrode reactions, particularly with organic substances, the rate determining step involves a smaller number of electrons than the overall reaction. Exchange current densities and transfer coefficients for the forward and backward reactions must then be introduced [cf. Vetter's review (15) and Oldham's analysis (18)].

The stoichiometric number first used by Horiuti is another kinetic parameter which is useful in the elucidation of mechanisms [see Bockris' review (19) for details].

<sup>1</sup> The survey of literature pertaining to this review was concluded in December, 1956.

<sup>2</sup> The coefficient  $\alpha$  is also used for anodic processes, particularly in the German literature.

## DETERMINATION OF KINETIC PARAMETERS

Kinetic parameters for electrode reactions are deduced from current-potential curves under conditions for which the interpretation is as simple and rigorous as possible. The simplest conditions are achieved when concentration polarization is avoided as, for instance, in most hydrogen overvoltage studies [see King's review (20) of cases in which concentration polarization was overlooked]. The exchange current and transfer coefficient are then readily obtained from the classical plot of overvoltage against the logarithm of current density. Concentration polarization cannot be prevented, even with vigorous stirring, for reactions with large exchange current densities; and there is partial or total control by mass transfer of reactants. If  $i_0$  is large enough, mass transfer is determinative, and the Nernst equation is obeyed for all practical purposes; the overvoltage cannot be measured, and the classical method of determining  $i_0$  and  $\alpha$  fails. These data can be obtained by relaxation methods under such conditions provided that  $i_0$  is not too large.

In relaxation methods, the response of the electrode to a perturbation from equilibrium (variation of potential or current) is followed for a short time (perhaps  $10^{-5}$  to 1 sec.), and concentration polarization is minimized but not eliminated. Three relaxation methods have been devised: the potential-step or potentiostatic method, the current-step or galvanostatic method, and electrolysis with superimposed alternating voltage. The development of these methods for fast electrode reactions is one of the significant advances in electrochemical kinetics during the last decade [cf. Gerischer (12, 21)].

*Potential-step method.*—In this method, the electrode potential which is initially at its equilibrium value is abruptly changed, and the current through the electrolytic cell is recorded. This method which is directly related to polarography was not applied to the determination of  $i_0$  and  $\alpha$  until potentiostats with fast control of potential were devised [Schön & Staubach (22)]. The method was developed by Gerischer & Vielstich (23). The exchange current is readily obtained from a linear plot of current against the square root of time. The transfer coefficient is determined from a log-log plot of the exchange current against the varying concentration of one reactant (see equation 1) according to a method first applied by Gerischer in A.C. electrolysis (24) and now commonly used in relaxation methods.

The technique is simplified and no potentiostat is needed when a voltage-step is applied to the electrolytic cell. The potential then changes continuously because of a varying ohmic drop, but this effect can easily be taken in account [Vielstich & Delahay (25)]. The determination of  $i_0$  and  $\alpha$  is essentially the same as for the potential-step method. The voltage-step method has the advantages of simplicity of technique and the elimination of reference electrode with all the difficulties resulting from the use of Luggin-Haber capillaries at high current densities (see *Experimental*). However, the capacity current interferes more in the voltage-step method than in the potential-step method.

The potential-step method has not been applied to electrode processes preceded or followed by a chemical reaction. The theory is available from polarographic studies (see *Polarography*), and application could be of interest for fast chemical reactions.

*Current-step method.*—This method is the counterpart of the potential-step method. A constant current is passed through the electrolytic cell, and the potential of the working electrode is recorded. The method was used for diffusion coefficient determinations about fifty years ago, but application to electrochemical kinetics is recent [Gierst & Juliard (26)]. Detailed and simple accounts of the theory are available [Delahay (27); Delahay & Mamantov (28)]. Exchange currents were first determined for markedly irreversible processes (27, 28), but faster processes were soon treated independently by Berzins & Delahay (29, 30), Feuillade (31), Lorenz (32), and Smutek (33). The current for the charging of the double layer is neglected in these treatments, but a complete treatment is also available [Berzins & Delahay (17)]. The exchange current is calculated from the linear plot of overvoltage against the square root of time, and  $\alpha$  is deduced from a log-log plot of  $i_0$  against the concentration of one reactant.

The current-step method has been applied to electrode processes preceded or followed by a chemical reaction (27). In fact, it was for a study of such processes that Gierst & Juliard (26) removed the method from oblivion. The theory of processes with coupled chemical reactions is well advanced and has been reviewed [Delahay (34); Gierst (35)]. The significant result, thus far, has been the study of slow chemical steps that precede the discharge of certain complex ions. Application to the kinetics of dissociation of weak acids (acetic, formic) has also been made (Delahay & Vielstich (36)).

*Electrolysis with superimposed alternating voltage.*—The electrode potential varies periodically by a few millivolts, and the alternating current through the cell is measured directly, or the cell impedance is determined with a bridge. The electrode behavior is described in terms of its equivalent circuit composed of a capacity and resistance in parallel or in series; and  $i_0$  is deduced from the variations of these elements of the equivalent circuit with frequency. The transfer coefficient, as in other relaxation methods, is deduced from the variations of exchange current with the concentration of one reactant [Gerischer (24)]. This method was the first of the relaxation methods to be applied to electrochemical kinetics, and the theory is well developed (12, 21, 27). Recent work has dealt primarily with applications, the derivation of a complete solution including transients (30), the extension to polarographic conditions, and the use of square waves.

In some applications, the preparation or handling (plugging of capillary electrode with alkali metal amalgams, etc.) of one of the reactants is difficult and it is convenient to prepare the reactant *in situ* by passing a direct current through the cell. The classical theory of the A.C. method, in which it is assumed that there is no steady direct current, is not applicable in all rigor. The concentration of the reactant produced by electrolysis decreases with

increasing distance from the electrode, but this gradient can be neglected as a first approximation: the diffusion layer is much thicker than the layer in which the concentration varies periodically with time. This approximate method was applied by Randles & White (37) to nickel ion discharge on nickel amalgam (very low solubility of nickel) in fused salts. Mathematical analyses of the method with superimposed direct current has been made: Breyer and co-workers [(38) and previous papers], Gerischer (39), Kambara (40), Koutecky (41), Matsuda & Ayabe (42), and Tachi and co-workers [(43) and previous papers]. The A.C. method with direct current component (A.C. polarography) is also useful in analytical determinations [see review by Breyer *et al.* (44)].

The interpretation of electrolysis with superimposed square waves is also well advanced [Kambara (45); Berzins & Delahay (30)]. The method does not appear more powerful in kinetics than the classical A.C. method, but it is of some interest in trace analysis because the effect of the capacity current can be minimized [Barker & Jenkins (46)]. Voltage square waves of large amplitude have been applied in the study of irreversible polarographic processes (see *Polarography*).

*Polarography and related methods.*—The determination of kinetic data for electrode processes by polarography has become possible in recent years. The problem is to calculate the rate of a heterogeneous reaction with mixed control by the electrochemical process and mass transfer of reactants. The first solution made use of the Nernst diffusion layer treatment, and a rigorous solution for the plane electrode was soon derived independently by several authors [see reviews (27, 47)]. The case of the dropping mercury electrode was analyzed by Koutecky (48) and, later, by Smutek (49), and Matsuda & Ayabe (50). Actually, Koutecky was concerned with another problem—the derivation of the limiting current for processes with a coupled chemical reaction—but his analysis can be transposed to slow electrochemical reactions (irreversible processes). These and related recent advances are briefly discussed below. Further information can be found in reviews (27, 47, 51, 52, 53) and bibliographies (54, 55, 56).

The current for an irreversible process (with a single rate determining step) at the dropping mercury electrode is a function of the dimensionless group  $\theta = [(k_f/D_{\text{Ox}}^{1/2}) + k_b/D_{\text{Red}}^{1/2}]t^{1/2}$ , where  $t$  is the time during drop life, the  $D$ 's are the diffusion coefficients, and the  $k$ 's are the rate constants for the forward and backward electrode reactions. The  $k$ 's are exponential functions of potential. Values of  $i/i_d$  ( $i$  current along the wave,  $i_d$  diffusion current) were tabulated by Koutecky (48) for instantaneous currents during drop life. The simple equation,  $i/i_d = 0.87\theta/(1 + 0.87\theta)$ , holds well for average currents. If the backward reaction can be neglected (for overvoltage exceeding 0.1 to 0.2 volt),  $\theta$  is a simple exponential function of potential, and a plot of  $\log [(i_d - i)/i]$  against potential is a straight line with a reciprocal slope proportional to the transfer coefficient  $\alpha$  [Kern (57)]. This reciprocal slope is smaller than its value for the corresponding reversible process (obeying the

Nernst equation)—a well-known fact which had never been accounted for satisfactorily before Koutecky's work.

The exchange current can also be deduced from the analysis of irreversible waves when the formal (standard) potential is known [Stromberg (58)]. If this is not the case, the irreversible process can be characterized by a rate constant at a reference potential, for instance, at  $E=0$  with respect to the normal hydrogen electrode. However, the latter procedure is less useful than the calculation of  $i_0$ . Koutecky's analysis of irreversible waves has been verified experimentally [Delahay & Mattax (59)].

A criterion for polarographic reversibility was deduced from kinetic considerations by determining under which conditions the equations for irreversible and reversible waves become identical [Delahay (60)]. It was found that polarographic reversibility corresponds to  $k_s > 10^{-2}$  to  $10^{-1}$  cm. sec.<sup>-1</sup> for all practical purposes. The backward reaction can be neglected under polarographic conditions for  $k_s < 10^{-8}$  cm. sec.<sup>-1</sup>. These limits are, of course, approximate. The dependence of the current (along the wave) on the head of mercury provides a simple experimental criterion for irreversibility [Kivalo, Oldham & Laitinen (61)].

Rate constants for chemical reactions coupled with electrode processes can be determined by polarography. These studies, which do not pertain directly to the determination of electrochemical kinetic data, are discussed here because of their importance on two counts: this was the first time (a) that kinetic considerations were introduced in polarography, and (b) that the method of Laplace transform for solving boundary value problems was used in the interpretation of electrode processes [Koutecky & Brdicka (62)]. The method of integral transforms is most fruitful and elegant in nonsteady electrolysis. Koutecky (63 to 66) greatly expanded the initial theory in which only first order processes and linear diffusion were considered. See also contributions of Brdicka (67, 68) and Wiesner (69), who did the pioneering work in this field; Koryta (66), Kivalo (70), Hans and co-workers [(71) and previous papers], and others (see 27, 68, 69). The main application has been the study of the dissociation-recombination process for weak acids or bases. A few other reactions have been studied, but in general, conditions for application of the polarographic method are not fulfilled. Data for acids studied thus far were reviewed by Brdicka (68). Iodic and bromic acids were recently studied by this method [Cermak (72)]. These studies dealt with weak acids with a reducible anion, but extension to nonreducible acids such as acetic acid has been made [Rüetschi (73); Delahay & Vielstich (36)].

Kinetic data for electrochemical processes can also be obtained by modified polarographic methods. The experimental conditions are more complex than for classical polarography and relaxation methods, and the chief value of the theoretical treatments of these methods is to provide a rational basis for their application to chemical analysis [Matsuda & Ayabe (74); Frankenthal & Shain (75); Matsuda (76); Kambara (45); Suzuki (77)].

The streaming mercury electrode is of some interest because contamina-



tion is minimized but is not very practical. The detailed hydrodynamic analysis of Weaver & Parry (78) and Koryta's simple treatment of irreversible processes (79) provide the necessary theory [see review of previous work in (27)].

*Radiotracer methods.*—The exchange between a metal and its cation has been studied by tagging one of the reactants with a radioactive isotope. The method which is not new [see King's review (80)] has the same limitation with respect to concentration polarization as the direct method of obtaining current-potential curves. Some features of the method are discussed by Losev (81) who applied it to the system  $\text{Zn}^{++}/\text{Zn}(\text{Hg})$ . Gerischer & Tischer (82) studied the couple  $\text{Ag}^+/\text{Ag}$ .

Radiotracers have been extensively applied to the deposition of less than an atomic layer of metal and to the study of electrode surfaces but this material is beyond the scope of this review [cf. Haissinsky (83) and Rogers (84)].

*Methods for coupled electrochemical reactions.*—In this case, the current for each process which cannot be measured can be obtained indirectly from the rates of appearance or consumption of some of the reactants. These rates are measured at several potentials, and a complete current-potential curve is obtained point by point. Of course, there can be partial or total control by mass transfer according to the  $i_0$ 's for the individual processes.

It is generally assumed that the net faradaic current is the algebraic sum of the currents for each process. This relationship is not rigorous, as was pointed out by Van Rysselberghe (7, 85) who developed a theory of electrode reaction coupling on the basis of Onsager's reciprocity relationships for coupled processes. It would be of interest to determine whether the coupling effect is sufficient to cause a detectable departure from the algebraic non-additivity of current. The nonadditivity of currents was reported for the simultaneous evolution of hydrogen and deposition of nickel on a nickel electrode, but this involves reactions on a continuously renewed surface and may not be truly a coupling effect [discussion of paper by Reiser & Fischer (86)].

*Comparison of methods.*—The conventional method for overvoltage studies or polarography is applied when  $k_s < 10^{-4}$  to  $10^{-5}$  cm. sec.<sup>-1</sup>. Somewhat faster processes can be studied by the classical method with vigorous stirring but relaxation methods are more advantageous. The classical method (without concentration polarization) is more advantageous than polarography: (a) the interpretation is not complicated by mass transfer considerations; (b) lower current densities can be utilized because the charging of the double layer does not interfere; and (c) electrode contamination can be minimized whereas this is not the case, in general, in polarography because of the addition of a maximum suppressor [cf. Bockris (87)]. Electrode contamination is the most serious of these drawbacks. Polarography, however, involves only simple technique, and approximate kinetic data supplied by this method may suffice for the elucidation of reaction mechanisms.

Among relaxation methods, electrolysis with superimposed alternating

voltage is the most precise because results are obtained from bridge readings rather than from oscillographic recordings. The method can be applied for  $10^{-8} < k_s < 1$  cm. sec. $^{-1}$ . The upper limit might be pushed somewhat but measurements become very difficult. The fastest reaction studied so far is the discharge of  $\text{Hg}_2^{++}$  on mercury [Gerischer & Staubach (88)]. The potential-step and current-step methods are applicable for reactions corresponding approximately to  $k_s < 1$  cm. sec. $^{-1}$ . The charging of the double layer and the error on the ohmic drop in the cell render application of the above three relaxation methods, in their present form, very difficult for  $k_s > 1$  cm. sec. $^{-1}$ . It is of interest to recall that  $k_s$  cannot exceed approximately  $10^3$  to  $10^4$  cm. sec. $^{-1}$  on the basis of collision considerations [Rubin & Collins (89)].

In the study of processes with coupled chemical reactions, relaxation methods are more powerful than polarography because the effect of diffusion is minimized. The interpretation for such processes in A.C. electrolysis is quite involved, and the potential-step and current-step methods can more readily be applied.

*Experimental.*—The electrode whose kinetics is studied must fulfill three important conditions: (a) it is essentially not contaminated; (b) the current density is the same over the whole electrode area; and (c) errors resulting from ohmic drop in solution are minimized. The first of these conditions is most easily fulfilled with mercury and amalgam electrodes. Three methods have been devised to produce mercury or amalgam electrodes of known area: (a) the use of a dropping mercury electrode with a synchronization device for measurement at a known stage of the drop life; (b) use of a hanging drop [Gerischer (90)]; (c) the formation of a drop of known volume with a microsyringe [Randles & White (37)]. Stationary drops obtained by the last two methods are more readily contaminated than the dropping mercury electrode. The effect of contamination can be further minimized, in some cases, by the determination of  $i_0$  and  $\alpha$  for different times of the drop life of a mercury drop, and by extrapolation to time zero. Careful preparation of solutions and, whenever possible, purification by pre-electrolysis is advisable [Bockris (19)]. Contamination of solid electrodes by oxide formation is avoided by sealing them in a glass envelope in a hydrogen atmosphere [Bockris *et al.* (91)].

The current density is uniform when the cell has the proper geometry and the electrodes are smooth. The first condition is quite easily fulfilled even for spherical or cylindrical electrodes, but smooth solid electrodes are not easily prepared. Small spheres obtained by melting are quite satisfactory [Graham (1); Bockris *et al.* (91)].

Errors resulting from ohmic drop in solution are easily corrected for at low current densities and high electrolyte conductance. A reference electrode with Luggin-Haber capillary may or may not be needed, but at any rate the position of the capillary tip is not critical. However, there are two possible serious errors at high current densities: (a) a large ohmic drop when the electrode tip is too far from the electrode; (b) shielding of the electrode with

the resulting local variation of current density when a tip of improper design is close to the electrode. These two errors are almost completely eliminated in the electrode tip with lateral canal designed and studied in detail by Piontelli and co-workers (92). Other designs of capillary tips have also been investigated [Eisenberg *et al.* (93)]. The Piontelli capillary tip is designed for plane electrodes, and application to small spherical electrodes (mercury) appears difficult. Conditions for spherical electrodes are particularly severe because the major fraction of the ohmic drop is in the immediate vicinity of the electrode.

In another method for minimizing the ohmic drop error, the electrode-tip distance is varied, and the potential is deduced by extrapolation. A detailed analysis of this method was made by Breiter & Guggenberger (94). Another alternative is the classical commutator technique, which was recently analyzed in detail by Scott (95).

Techniques for electrolysis with molten salts up 200° to 300° are similar to those for aqueous solutions [Randles & White (37)], but serious difficulties are encountered at higher temperatures because of destruction of the cell materials. Many designs are discussed in the technical literature. Cells for the precise determination of current-potential curves are described by Piontelli and co-workers (96) and references therein.

Instrumentation for the determination of current-potential curves has become classical. Techniques in relaxation methods are mentioned in some of the papers previously quoted. Further reference is made to the following papers: an A.C. bridge [Randles (97)], a resonance method for impedance measurement [Watanabe, Tsuji & Ueda (98)], recording of impedances [Schön, Mehl & Gerischer (99)], experimental methods for the current-step method [Delahay & Mattax (100); Gierst (101); Reilley, Everett & Johns (102)], methods for the measurement of Volta potentials [Möhning (103)], and an improved instrument for periodic square wave variation of current [Fischer, Seipt & Morlock (104)].

#### MECHANISMS AND INTERPRETATION OF KINETIC PARAMETERS

The correlation of kinetic parameters to fundamental concepts raises many problems: (a) effect of electrode material for a given reaction; (b) effect of medium for given reaction and electrode; (c) correlation of parameters for different substances of a series, etc. Results are often presented as plots of kinetic data against some characteristic parameter. The exchange current or  $k_s$  is plotted rather than the overvoltage at a given current density or the polarographic half-wave potential (for irreversible processes) because the latter data depend on  $\alpha$  whereas  $i_0$  and  $k_s$  do not. However, the determination of  $i_0$  or  $k_s$  may require a long extrapolation for markedly irreversible reactions, and a small error on  $\alpha$  may cause an appreciable error on  $i_0$  and  $k_s$ . Half-wave potentials or overvoltage for given conditions then are more reliable than  $i_0$  or  $k_s$  for correlation purposes provided that  $\alpha$  is essentially constant.

*Hydrogen evolution and oxidation.*—Reliable kinetic data are now available for hydrogen evolution on many metals, and the present trend is toward the correlation of these data. However, uncertainty—even minor—in the extrapolation of data is occasionally the source of a controversy [Horiuti & Sugawara (105) versus Bockris & Potter (106)]. Anion adsorption is a source of difficulty which is now well understood [Bune & Kolotyrkin (107)]. A detailed review appeared in this series (19), and further details can be found elsewhere [Knorr (108); Vetter (109)].

In general, mechanisms of discharge have been elucidated from the variations of overvoltage with current density and the use of the stoichiometric number. The latter quantity is not easily determined for metals with high overvoltages, and nonsteady state electrolysis can then supplement the classical method [Gerischer & Mehl (110); Breiter, Knorr, *et al.* (111, 112)].

Recent interpretations of the effect of electrode material are based on two rather old ideas: the dependence of overvoltage on the work function of the electrode [Wirtz (113)] and the heat of adsorption of hydrogen [Horiuti & Polanyi (114)]. The heat of hydrogen adsorption is the more significant quantity, and the dependence of overvoltage (or  $i_0$ ) on electrode characteristics such as work function, lattice constants, compressibility, etc., can be correlated to the effect of these quantities on the heat for hydrogen adsorption as was pointed out by Rüetschi & Delahay (115). These authors considered only control by slow discharge but other mechanisms must also be taken into account [Conway & Bockris (116); Gerischer (117); see also Oikawa (118) and Vasenin (119)].

The electrolytic oxidation of hydrogen has received relatively little attention. Frumkin & Aikazyan (120) made the interesting observation that the current first increases and then decreases at more anodic potentials because of anion adsorption. This effect was accounted for quantitatively.

*Oxygen evolution and reduction, and hydrogen peroxide.*—Fewer kinetic data for electrolytic oxygen evolution are available than for hydrogen, and only two metals (Pt, Co) were recently investigated [Bockris & Shamshul Huq (121); Tur'yan & Gershkovich (122)]. Possible mechanisms were studied in detail by Bockris (123) by the Christiansen method for consecutive reactions. If  $\text{OH}^-$  discharge is rate determining, overvoltages for different metals  $M$  are directly related to the  $M\text{—OH}$  bond energies [Rüetschi & Delahay (124)]. The effect of the degree of oxidation of the electrode can be interpreted from variations of this bond energy [Yefimov & Izgaryshev (125)]. The isotopic effect in oxygen evolution was interpreted by Anbar & Taube (126).

The mechanism of oxygen electrolytic reduction has received much attention for graphite electrodes in alkaline medium because of practical implication in battery and fuel cell technology. An elegant study of this reaction by oxygen-18 tagging was made by Yeager and co-workers (127). They concluded (a) that all the oxygen in the peroxide ion  $\text{HO}_2^-$  comes from the oxygen gas and not from water; and (b) that the oxygen bond is not broken

in the formation of  $\text{HO}_2^-$ . This suggests the formation of  $\text{O}_2^{--}$  as intermediate and the subsequent addition of  $\text{H}_2\text{O}$  to  $\text{O}_2^{--}$  with production of  $\text{HO}_2^-$  and  $\text{OH}^-$  ions. Other electrode processes involving hydrogen peroxide, and especially the catalytic decomposition of this substance on platinum, have also been investigated [Bockris & Oldfield (128); Gerischer & Gerischer (129); Winkelman (130)].

*Electrocrystallization.*—Amalgam electrodes are the simplest and most reliable electrodes for correlation of factors involved in metal ion discharge. The process of surface formation is avoided, but since the process is of significance, investigations with solid electrodes are of great interest. Crystallization of metals at electrodes has been studied in detail, and it has been observed that surface diffusion of the metal atoms contributes an overvoltage component [Fischer (3, 131); Lorenz (132); Sroka & Fischer (133)].

*Discharge of metallic complexes.*—New experimental methods have now become available for the elucidation of the discharge of metallic complexes. The exchange current density for each species being discharged can be computed from measurement of  $i_0$  for a varying concentration of complexing substance [Gerischer (134)]. The method involves the assumption that equilibrium between the different complexes is frozen, but this simplification is quite valid at concentrations of complexing agent at which only a single species is very much in excess. Exchange current densities are generally obtained by relaxation methods, but classical methods and polarography can also be applied [Stromberg & Ivanstova (135)] whenever the  $i_0$ 's are low enough.

The occurrence of a chemical step before the discharge of certain complexes is quite well established. This point was debated for years [cf. Parry & Lyons (136)], but rather conclusive evidence was only recently obtained by the current-step method for the discharge of  $\text{Cd}(\text{CN})_4^{--}$  [Gierst & Juliard (26)]. A theoretical treatment for the calculation of rate constants was subsequently given by Delahay & Berzins (27), and application to  $\text{Cd}(\text{CN})_4^{--} = \text{Cd}(\text{CN})_3^- + \text{CN}^-$  was made by Gerischer (137). Other complexes have been studied (27, 34).

Data for  $\text{Cd}(\text{CN})_4^{--}$  indicate that the rate constant  $k_s$  at the equilibrium potential for each species decreases from  $\text{Cd}(\text{CN})_2$  to  $\text{Cd}(\text{CN})_4^{--}$ . In fact,  $k_s$  for the latter species is so low that reduction via dissociation into  $\text{Cd}(\text{CN})_3^-$  is more rapid than direct reduction. It would be tempting to generalize these observations on the charge effect, but further experimental evidence is needed.

Correlations between  $i_0$  values for a given metal and different complexing agents have not been established thus far. Some progress has been made by consideration of the electronic configuration of the complex, and one important conclusion has been reached, namely that complexes which do not undergo an electronic rearrangement have large  $i_0$ 's [Lyons (138); Vlcek (139)].

*Molten electrolytes.*—The discharge of metal ions in molten electrolytes

is generally controlled by mass transfer [Piontelli *et al.* (96, 140)] even for amalgam electrodes in low melting eutectic mixtures (100–200°). Values of  $k_s$  ( $< 0.2$  cm. sec.<sup>-1</sup>) have only been reported thus far for nickel ion discharge on nickel amalgam [Randles & White (37)]. A.C. electrolysis has been applied for solid metallic and graphite electrodes but quantitative interpretation is difficult [Drossbach (141); Laitinen & Osteryoung (142)]. Since the overvoltage not due to concentration polarization is negligible, electrolysis in molten salt only supplies information that, in principle, can be obtained by potentiometry.

Perhaps more successful, but still of limited scope, is the measurement of limiting currents or transition times<sup>a</sup> with mass transfer control [cf. Drossbach's treatment (143)]. Diffusion coefficients can be obtained in this manner, and abnormalities in their values or temperature dependence can be detected [Kolk *et al.* (144); see also Chovnyk (145)]. Altogether, electrolysis is not a powerful tool for the study of the physical chemistry of molten electrolytes; conductance and viscosity studies and other methods are more fruitful.

*Reduction and Oxidation of Anions.*—Current-potential curves for the reduction of certain anions at low concentration of supporting electrolyte exhibit a minimum in the limiting current at potentials negative with respect to the point of zero charge [cf. Frumkin's review (146)]. These observations were interpreted by Frumkin & Florianovich, and other authors [see (148) for references] as a result of the effect of potential on anion repulsion from the electrode and variations in the rate of electron transfer. Frumkin & Florianovich improved their original treatment by taking into account concentration polarization at the electrode (147). Their treatment does not account for the observations made by Kivalo & Laitinen (148), who consequently advanced another explanation based on the oxidation of mercury by the reducible anion. The latter process, however, appears quite difficult in the range of potentials being considered, and, furthermore, minima are observed with other metallic electrodes than mercury. At any rate, the work of Kivalo & Laitinen indicates that the treatment of Frumkin & Florianovich does not cover all the cases of minima observed thus far. This problem is now being attacked by Frumkin (146) on the assumption of electron transfer by tunnel effect. An indication of a possible tunnel effect is the very low temperature coefficient of the limiting current in the range of the minimum.

Mechanisms of anodic oxidation of anions have been reinvestigated: sulfate [Frumkin *et al.* (149)], chlorate [Philips & Morgan (150)], and oxalate [Llopis & Guillen (151)]. The study of peroxydisulfate formation is a good example of the use of isotope tagging for the elucidation of mechanisms. It was concluded that  $S_2O_8^{--}$  is formed by combination of two intermediate

<sup>a</sup> The transition time in the current-step method is the counterpart of the limiting current in the potential-step method. The concentration of reducible or oxidizable species become equal to zero at the transition time as the potential varies in an electrolysis at constant current in unstirred solution.



ions  $\text{SO}_4^-$  and not by oxidation of  $\text{SO}_4^{--}$  by oxygen. Such experiments are meaningful only when isotope exchange does not interfere.

*Organic substances.*—Only correlations of polarographic half-wave potentials by the Hammett equation and quantum mechanical calculations will be mentioned here [for reviews of other material see Wawzonek (53) and Swann (152)]. Such correlations hold for reversible systems, i.e., for cases in which half-wave potentials are practically equal to the standard potentials. Extension to irreversible systems is permissible when the over-voltages and the products of the transfer coefficient by the number of electrons involved in the activation step are the same for all the substances being compared.

Since these correlations are not really within the realm of electrochemical kinetics, reference is made to the recent literature (153 to 158) without further comment.

#### ADSORPTION

Three problems involving adsorption on electrodes will be discussed: (a) adsorption without electrode reaction; (b) electrode reaction involving an adsorbed substance; (c) electrochemical reaction at an electrode covered with a foreign substance that is not reduced or oxidized. Reference is made to two reviews by Frumkin (146, 159).

*Adsorption without electrode reaction.*—The adsorption equilibrium and the kinetics of adsorption raise two fundamental problems. Adsorption equilibrium was studied by Frumkin and Butler some thirty years ago, and was recently reinvestigated by Hansen, Minturn & Hickson (160). The surface coverage in Frumkin's treatment was expressed by these authors in terms of the differential capacity of the double layer to allow experimental study of the dependence of coverage on concentration and potential. Theoretical coverages, which however contain adjustable parameters, agree with experimental values. In general, there is desorption at sufficiently anodic potentials because of strong anion adsorption; and the range of desorption potentials for a given substance depends on the anion [Breyer & Hacopian (161); see Miller & Grahame (162) for polyelectrolytes].

Little is known about the kinetics of adsorption of organic substances on electrodes except that the process is diffusion controlled for mercury and the substances studied so far (mainly aliphatic alcohols) [see Grahame's review (1)]. Two treatments are available for the application of the alternating current method to adsorption kinetics with simultaneous control by diffusion and adsorption, but applications have been limited to cases with pure diffusion control [Berzins & Delahay (163); Lorenz & Möckel (164)]. Cases with mixed control might well be found with solid electrodes, but interpretation would not be straightforward in view of the difficulties plaguing differential capacity measurements with solid electrodes [Grahame (1); Lorenz (165)]. The results of Hackerman & Brodd (166), who were able to



obtain reliable differential capacities for a series of metals, are encouraging in this respect.

Adsorption kinetics with pure diffusion control was recently treated for the plane electrode, the dropping mercury electrode, the streaming mercury electrode, and electrodes in stirred solution [Delahay & Trachtenberg (167)]. Adsorption with diffusion control is a slow process that may in some cases require 30 min. or longer to reach equilibrium. As a result, adsorption measurements with the dropping mercury electrode can be in error because of nonattainment of equilibrium at least for dilute solutions.

*Electrode process involving an adsorbed species.*—Such processes may be quite common although the effect of adsorption is undetected in general. A treatment for the current-step method, based on a simplified linearized isotherm, was given by Lorenz (168, 169). The transition time is longer than for a purely diffusion controlled process. An analysis of A.C. electrolysis for processes with adsorbed species was developed by Laitinen & Randles (170). The equivalent circuit has an additional series resistance and capacity in parallel with the usual polarization resistance and capacity.

*Electrode reactions with an adsorbed foreign substance.*—In general,  $i_0$  and  $\alpha$  decrease as a result of adsorption of a foreign substance such as a polar organic substance. Because of the decrease in  $i_0$  and  $\alpha$  and the increase in actual current density, current-potential curves such as polarographic waves become more irreversible upon addition of an adsorbable substance. If  $i_0$  is high enough,  $k_s$  still corresponds to reversible behavior ( $k_s > 10^{-1} - 10^{-2}$  cm. sec.<sup>-1</sup>), and the effect of adsorption is undetectable by polarography, although it is readily observed in relaxation methods. For systems with a sufficiently low  $i_0$ , the distortion of waves can be very pronounced. An account of the evolution of these ideas is given by Frumkin (159), and further experimental proof of their validity has been advanced (171 to 175).

Adsorption of a mixture of two substances has an interesting effect when the more strongly adsorbed substance (gelatin) is less effective than the other substance (camphor) in making the electrode reaction [ $\text{Cd}^{++}/\text{Cd}(\text{Hg})$ ] more irreversible. The addition of gelatin to a solution of  $\text{Cd}^{++}$  ion containing camphor then decreases the overvoltage because of displacement of the camphor by gelatin [Zagainova & Stromberg (176)].

The effect of adsorption of certain alkaloids and amines on hydrogen overvoltage is peculiar in that the overvoltage may be decreased or increased. Two competitive effects are involved: increase of overvoltage because of adsorption of alkaloid, and decrease in overvoltage because the alkaloid is a better proton donor than  $\text{H}_3\text{O}^+$ . A detailed analysis was made by Conway, Bockris & Lovrecek (177). These ideas could be applied to the observations of Andreeva (178) on the effect of certain amines on hydrogen overvoltage.

Adsorption of a foreign substance also causes a decrease in limiting current or transition time because of "blocking" of the electrode surface. The

surface concentration of adsorbate varies with potential, and the dependence of limiting current on potential is complex. Furthermore, in polarographic measurements adsorption equilibrium may not be attained at the dropping mercury electrode. It is customary in such studies to investigate the dependence of limiting current on the concentration of adsorbate, but the surface coverage is a more rational variable than concentration. Further progress could be made by characterizing the "blocking" of the electrode by a rate constant which could be determined by the current-step or the potential-step method.

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# KINETICS OF REACTIONS IN GASES<sup>1,2</sup>

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## INTRODUCTION

In the study of reaction rates, the purpose is often qualitative description. A pioneering investigation may seek general information about a wide range of substances, or it may seek a qualitative mechanism, that is, a list of reasonable-looking elementary reactions with plausible reactive intermediates, which is adequate to explain observations. This aspect of kinetics and mechanisms is extremely important and is often all that is needed.

A quite different aspect of the science is that of quantitative mechanisms. One attempts to get the rates of the separate elementary steps, and the numerical values for the rate factors,  $A$  and  $E$  of the Arrhenius equation<sup>4</sup>

$$k = A \exp (-E/RT) \quad 1.$$

Spectra, structure, and thermodynamic data are obtained for the free radical and other intermediates wherever possible. This emphasis on numbers is based on the assumption that for elementary reactions, data are transferable from one system to another; for example, rate factors for an elementary reaction found in the photolysis of acetone may be used to characterize the same elementary reaction in the decomposition of ethane, or in an internal combustion engine, or in a flame, or wherever it is found. Trotman-Dickenson (1) has treated gas kinetics almost entirely from this point of view and has presented extensive tables of values of rate factors for results through 1954. When there are sufficient lists of rate factors, bond energies, and free radical structures, the problem of reaction mechanisms largely will be reduced to looking up all appropriate entries in a handbook. This state of affairs is still far in the future, although below a few definite cases will be pointed out.

A third field of experimental kinetics is apparent: the investigator singles out some system, perhaps one worked on several times before, in which one or more elementary reaction rates can be separated out or measured directly. Carefully, quantitative data are obtained to test theories of reaction rates. Great care is exerted to exclude effects of side reactions, surface reactions, or other spurious effects. In the field of qualitative mechanisms, the investigator may be primarily interested in the substances; in the third field, the substances are of no interest; concern is with the phenomenon. The second field serves both the first and the third: quantitative considerations are the

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<sup>4</sup> Throughout this review, units of  $A$  are  $\text{sec}^{-1}$  for first-order,  $\text{cc. mole}^{-1} \text{sec}^{-1}$  for second-order, and  $\text{cc.}^2 \text{mole}^{-2} \text{sec}^{-1}$  for third-order reactions; units of  $E$  are  $\text{kcal./mole}$ .

best way to establish the correct descriptive mechanism, and precise quantitative data are the only ones on which to test a theory.

In this review, first emphasis will be given to recent data used as a test of theory. Next, there is a section on mechanisms established by use of quantitative rate factors, and also a partial list of new rate factors reported this year. There is a section on qualitative mechanisms for a few cases which happen to interest the reviewer. Finally, there is a small section on recent developments in experimental techniques. Many rate studies of high caliber are omitted because they do not happen to fall into the categories selected. For a complete listing of articles in kinetics, there is, of course, a convenient source (2).

#### EXPERIMENTAL DATA IN THE TEST OF THEORY

Several articles have appeared this year which tested the activated complex theory (3) against experimental data, for most of these a series of similar reactions was considered, and care was taken to make any arbitrary assumptions uniform for the entire series. In each case one must ask whether a comparison of this sort is a test of the general theory itself or a test of the model used for the activated complex or a test of the simplifying assumptions made in carrying out the computations or even a test of the reliability of the experimental data. Before pointing out examples where each of these interpretations may be given, it seems worthwhile to review very briefly certain aspects of the general theory and the detailed models.

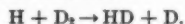
With respect to the activated complex there are four rates of interest: (a) the rate of formation of activated complexes from reactants, (b) the rate of formation of activated complexes from products, (c) the rate of decomposition of activated complexes to give reactants, and (d) the rate of decomposition of activated complexes to give products. At total chemical equilibrium between reactants and products,  $R_a^0 = R_c^0$  and  $R_b^0 = R_d^0$ , where superscript zero denotes equilibrium. For the initial rate of a reaction  $R_b = 0$ ,  $R_a = R_c + R_d$  from which it follows: rate of reaction  $= R_d = R_a - R_c = R_a[R_d/(R_c + R_d)] = \kappa R_a$ . If during reaction the reactants have about the same distribution over excited states as at equilibrium, then the rate with which excited reactants reorganize themselves to produce the activated complex is the same during reaction as during chemical equilibrium, or  $R_a = R_a^0$ . But since  $R_a^0 = R_c^0$ , then  $R_a$ , with reaction, is equal to  $R_c^0$ , at chemical equilibrium. Within the framework of the general activated complex theory, there are two radically different methods of calculating the same thing, the rate of reaction,  $\kappa R_a$  or  $\kappa R_c^0$ . By the first method one calculates the rate of formation of activated complexes by summing over all manners with which excited reactants, with an equilibrium distribution, move into the configuration of the activated complex. This procedure of computation is named the "dynamic" method; collision theory is a crude form of the dynamic method, and Slater's (4) classical theory of unimolecular reactions is a more detailed example of a dynamic calculation. On the other hand one can calculate the

rate of formation of activated complexes as the microscopic reverse of their rate of decomposition at equilibrium. This method leads (3) to:  $k = \kappa K' c$ , where  $c$  is the unimolecular rate constant for decomposition of the activated complex,  $K'$  is the equilibrium constant for the activated complex, and  $\kappa$  is the transmission coefficient. The nature of the potential energy maximum along the reaction coordinate is important in the further development of the theory (5). If the top of the pass is highly structured, the transmission coefficient is an important term, variable from reaction to reaction. If the top of the pass is extremely sharp, then the unit cell of area  $h$  in phase space is narrow in  $q$ , high in  $p$ , leading to large and uncertain zero point energies and tunnel effects (5). If the top of the pass is not sufficiently flat, then the reaction coordinate is coupled to other degrees of freedom, and it is not sufficiently separable to give a simple general rate expression. If the top of the pass is sufficiently broad, flat, and unstructured, then  $k = \kappa (kT/h) K^\ddagger$ . The crucial assumption does not concern equilibrium, but rather it concerns the generality with which the reaction coordinate is separable and free from effects of detailed structure, reflections, etc. (5).

When the representative point for the reaction coordinate lies within its unit cell of phase space, the rest of the activated complex may be in any and all states accessible to it. Thus the rest of the complex will be like a normal molecule at the reaction temperature; mostly, each degree of freedom will be in energy states near  $kT/2$ , although there will be the usual Boltzmann factor of excited motions. Since the rest of the activated complex, other than the one-dimensional reaction coordinate, is in a normal state, it will have normal bond lengths, normal force constants, normal barriers to internal rotation, etc. Thus, the usual theories and empirical rules of molecular structure and molecular spectroscopy apply to the activated complex. If one can calculate or measure the energy of the reaction coordinate, the rest of the problem follows in familiar terms. The computation of the rate of reaction from considerations of structure and force constants, and thus the equilibrium constant, of the activated complex is referred to as the "structural" method of the activated complex theory.

If one could accurately calculate from quantum mechanics the structure and properties of the activated complex, every test of reliable experiment against theory would be a test of the theory itself. Actually one uses simplified physical models for the activated complex and mathematical approximations in the computations. A good or poor agreement with experiment for an unrealistic model neither proves nor disproves the validity of the general theory.

*Bimolecular reactions.*—It is a great pity to test powerful theories against erroneous experimental data; prior to this year that was exactly the situation for the simplest of all chemical reactions

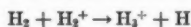


A model of how one should comprehend and master all pertinent experimental variables, how one should consider all aspects of mechanism, and how

one should set up the theoretical model and carry out the computations is given by Boata *et al.* (6) in their careful study of the exchange reaction between hydrogen and deuterium. They found that oxygen diffuses through silica at 1000°K., even after prolonged degassing, to give an error of approximately 100 per cent in the measured rate [the mechanism of this oxygen-induced deuterium exchange was studied in detail by Klein *et al.* (7)]. Boata *et al.* enclosed the silica reaction flask in an outer flask which was continuously evacuated; temperature was measured by a coaxial insert into the reaction bulb. In the mechanism all steps and their reverse were considered, and no processes were neglected just for mathematical expediency. Rates were measured at high temperatures, 916 to 1010°K., one parameter in the structural method of the activated complex theory was fixed to agree with experiment at the highest temperature, and with no further adjustment of parameters experiment was compared with theory between 500 and 1000°K. by use of literature data at the lower temperatures. Whereas previous tests of activated complex theory against experimental data over the wide temperature range were in serious disagreement, in the present case with the elimination of errors due to diffusion of oxygen through the silica, the agreement between theory and experiment over a 500° temperature range was completely satisfactory. In summary, this test of activated complex theory was not an absolute one since one parameter was adjusted from the data; it may, however, be interpreted as strong confirmation of the theoretical form of the entropy of activation.

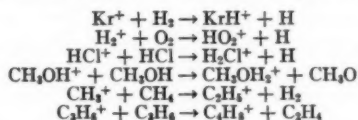
For bimolecular associations and for many gas phase ion-molecule reactions, there is very little activation energy, and it arises from the easily computed centrifugal distortion of the complex. For these cases the calculation of essentially the entropy of activation in the usual way gives an absolute value for the rate. Shepp (8) refined the rotating sector theory, and application of the theory to data in the literature gave  $2.2 \times 10^{13}$  cc. mole<sup>-1</sup> sec.<sup>-1</sup> for recombination of methyl radicals. By the same method, Ayscough (9) found  $2.3 \times 10^{13}$  cc. mole<sup>-1</sup> sec.<sup>-1</sup> for recombination of trifluoromethyl radicals; calculations by Gorin's (10) method of the activated complex theory gave  $1.7 \times 10^{13}$  cc. mole<sup>-1</sup> sec.<sup>-1</sup> for CF<sub>3</sub> at 400°K., which is in excellent agreement with experiment.

For a long time it has been obvious that reactions between ions and molecules in the gas phase must be important in many processes, for example, radiation chemistry (11, 12, 13), electric discharge reactions (14), photochemistry in the far ultraviolet (15), reactions in the upper atmosphere (16, 17), microwave pulses (18), shock waves (19), and flames (20). Twenty years ago, Eyring, Hirschfelder & Taylor (21) derived rate expressions for ion-molecule reactions and evaluated the rate constant for



From time to time special methods [for example (22, 23)] have been used to accelerate ions into a reaction chamber where elastic and inelastic scattering

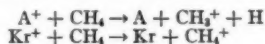
(charge transfer, excitation, and dissociation) have been observed; however, these data have not been such as to constitute a general solution to the problem of ion-molecule reactions. The products of ion-molecule reactions in the mass spectrometer have been recognized for several years, for example,  $\text{CH}_5^+$  (24),  $\text{H}_3^+$  (25), etc.; often these reactions have been regarded as nuisances and hazards to the correct identification of mass spectra. However, in 1955 (26), and again this year (27), Stevenson & Schissler turned the emphasis around and showed how to measure with 2 per cent precision the second-order rate constant or the reaction cross section for 21 reactions, such as



This important work has been taken up and checked in several other laboratories. Meisels, Hamill & Williams (28) confirmed Stevenson's results for the reaction



They showed a difference between argon and krypton

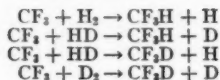


Field, Franklin & Lampe (29) also confirmed Stevenson's results and added interesting new cases, such as,



In addition these authors, following Eyring *et al.* (21), presented a general formula for the cross section of such reactions. These cross sections calculated on an absolute basis are in quite satisfactory agreement with experimental values, both for structurally simple and very complex reactants. The significance of these investigations is twofold: on the one hand these represent an impressive confirmation of reaction rate theory, and, on the other hand, the experimental values obtained and the theory may be used to predict practical numbers for the many fields of work listed in the first sentence of this paragraph.

In this review last year, Porter (30) gave a summary of the status of recent calculations based on potential energy surfaces constructed in the usual manner from Morse functions and an assignment of the fraction of the coulombic integrals (3). Usually, the calculation of activation energy by this method is unsatisfactory on a quantitative basis, and also some qualitative features are probably incorrect, namely, the well in the top of the pass. By this method, however, one can get an estimate of the lengths of bonds in the critical configuration and the force constant for the symmetric stretching mode for three center reactions. This procedure was followed by Ayscough & Polanyi (31) for the series of reactions



For these four reactions the rate constants at 400°K. were respectively 4.49, 1.10, 0.564, and  $0.762 \times 10^6$  cc. mole<sup>-1</sup> sec.<sup>-1</sup>, and the activation energies were  $9.5 \pm 0.7$ ,  $10.5 \pm 1.5$ ,  $10.2 \pm 1.5$ , and  $10.2 \pm 0.7$  kcal. Potential energy surfaces were constructed for a three-center reaction, treating the CF<sub>3</sub> group as one atom. In the vibration analysis, vibrations of CF<sub>3</sub> in the activated complex were cancelled against vibrations of CF<sub>3</sub> as a reactant, stretching modes of (CF<sub>3</sub>)—H—H were neglected, the two degenerate C—H—H bending frequencies were estimated by analogy with other molecules, and apparently the F—C—H bending modes were neglected (a serious omission). For the first reaction the calculated pre-exponential factor is about one-half the observed one. In view of the crudity of the vibrational analysis and uncertainty in activation energy, this agreement is about all one could expect; and the finer points of the series of isotopic reactions cannot be exploited.

Correction of an error in deductions from published data (32), led to an improvement between theory and experiment for eight different isotopic species with various substitutions for deuterium in the reactions between methyl and hydrogen (33).

For complex reactions such as CH<sub>3</sub>+H<sub>2</sub>, CH<sub>3</sub>+C<sub>6</sub>H<sub>14</sub>, NO+O<sub>3</sub>, NO<sub>2</sub>Cl+NO, NO<sub>2</sub>+F<sub>2</sub>, etc. it is desirable to have a quick simple method for assigning approximately correct bond distances, force constants, and barriers to internal rotation in the activated complex. The construction of potential energy surface is forbiddingly complicated, especially since multidimensioned surfaces must be found even to evaluate the very important bending force constants adjacent to the transferred atom in a three-center reaction. Such a quick, simple, approximate method of determining the structure and mechanical properties of activated complexes was presented by Herschbach *et al.* (34) for reactions between the oxides of nitrogen, ozone, fluorine, etc. This method was extended by Wilson & Johnston (35) to treat hydrogen atom transfers in atom and free radical reactions with organic compounds, and it was used by Johnston, Bonner & Wilson (36) in the study of the C<sup>12</sup>—C<sup>13</sup> isotopic reaction NO<sub>2</sub>+CO→NO+CO<sub>2</sub>. Pitzer (37) has shown how the method can be simplified even further for reactions between a large molecule and an atom.

This method can be expressed in terms of a series of formal rules. (a) The relative positions of atoms in the complex are determined by the consideration of equivalence with respect to forming reactants or products. (b) Valence bond structures are written for all resonance forms of the activated complex; this may involve resonance of single bonds and "no bonds" for certain atom pairs; by averaging the bond orders over these structures an order is assigned to each bond, fractional bonds being permitted. One uses Pauling's (38) simple rule for the length of a bond of any order relative to its single bond length; single bond lengths are based on the sum of the covalent radii.



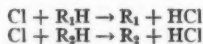
Rigid rotator partition functions may be found from this model. (c) Stretching force constants are assigned from Badger's rule (39) and the bond length as computed above. Bending force constants are assigned by analogy with corresponding structures of stable molecules. (d) By means of the straightforward group-theoretical treatments of Wilson, Decius & Cross (40) one identifies the internal motions of the complex, classifying them as light atom stretch, light atom bend, heavy atom stretch, heavy atom bend, internal rotation, and reaction coordinate. For atom transfer reactions the reaction coordinate is taken as the antisymmetric stretch of the atom transferred with an interaction term which reduces to zero the restoring force on this motion. Similarly the internal motions of the reactants are analyzed as to class. Whenever a reactant has an internal motion in the same class as the activated complex, these terms are cancelled without being calculated. Extensive cancellation is usually possible, and this is the simplifying feature of this method. However, one must be very careful not to cancel motions of different classes; for example, a stretching vibration against a bending vibration. Also, vibrations intimately associated with the reaction coordinate are not cancelled. Vibrational frequencies which cannot be cancelled are evaluated in the usual manner (40); typically, even for very complicated reactants, the vibration problem to be solved is equivalent to that of a molecule with only three, four, or five atoms. For more approximate work the frequencies may simply be assigned by analogy with frequencies of the same class from comparable stable molecules. (e) Moments of inertia for internal rotations are computed by the simple method described by Herschbach *et al.* (34). The most serious shortcoming to this set of rules is its inability to evaluate barriers to internal rotation. For the cases treated so far, it can be argued that the entropy of the entire complex is best represented by allowing free internal rotation about the reaction coordinate. This does not imply that the complex has time to rotate during its brief period at the top of the pass; but rather that when the reaction coordinate has the configuration represented by a point at the top of the barrier, the rest of the complex may equally well have any configuration represented by the internal rotation. For other non-cancelling internal rotations, one may try to estimate barriers from the potentials given by Mason & Kreevoy (41). (f) Electronic degeneracies are assigned from considerations of reactants and products; a factor of three uncertainty between singlet and triplet complexes arises in some cases. By virtue of uncertainty with respect to bending force constants, barrier to internal rotation, and electronic degeneracy in some cases, this method is useful primarily as an order of magnitude evaluation of pre-exponential factors.

For 12 reactions between the oxides of nitrogen, oxyhalides of nitrogen, chlorine oxides, ozone, fluorine, etc. the agreement between calculated and observed pre-exponential factors was within about an order of magnitude in all cases except one. (Simple collision theory was systematically high by about two or three powers of ten.) Most of these reactions were extremely fast exothermic reactions with a substantial uncertainty in activation energy.

Thus, this theoretical model by way of activated complex theory agrees with experiment within the expected range of errors except for one case; since the method worked so well for 11 similar cases it is proposed that this one is seriously in error. One of the conclusions for this series is the very great importance of low frequency vibrations and internal rotations in the polyatomic activated complexes. If these degrees of freedom are neglected, as is sometimes advocated for extremely simple considerations, the error would be a factor of 500 for the reaction  $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$  at dry ice temperature and a factor of  $6 \times 10^5$  for  $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$  at  $550^\circ\text{K}$ . As one goes from atoms to linear molecules to nonlinear molecules for reactants, one expects (3) a decrease in pre-exponential factor since classical rotational partition functions are replaced by quantized vibrational partition functions. However, this expected decrease is partially compensated by the appearance of more or less free internal rotations and low frequency bending oscillations in complicated activated complexes. The discrepancy between simple collision theory and experiment is more nearly a factor of  $10^2$  or  $10^3$  than the otherwise expected factor of  $10^8$  or  $10^{10}$ . Normal pre-exponential factors for two nonlinear reactants are about  $10^{11}$  cc. mole $^{-1}$  sec. $^{-1}$ , not  $10^8$  to  $10^9$ .

The experimental data for reactions between methyl radicals and halogen atoms with organic molecules are considerably more precise than the reactions of the oxides of nitrogen. Correspondingly greater attention needed to be given to bond distances near the atom transferred, and careful evaluation of bending frequencies  $\text{R}-\text{H}-\text{C}$  as well as  $\text{H}-\text{C}-\text{H}$  in the complex  $\text{R}-\text{H}-\text{CH}_3$  was required (35). For reactions with no skeletal internal rotations, calculated and observed pre-exponential factors were in excellent agreement. For reactions with skeletal internal rotations treated as if free, calculated values were higher by a factor of 2 or 4 than the observed ones, perhaps implying that fairly strong barriers to internal rotation should have been used. Here, too, one case treated was so far out of line with the rest that the authors recommended an experimental reinvestigation.

Knox & Trotman-Dickenson (42) proposed a sensitive test of activated complex theory by computing ratios of *A*-factors for a series of reactions of the type



since experimental data of high accuracy were available for these rate ratios. This was an excellent idea, but unfortunately the authors neglected internal rotations and vibrations because they argued that differences in these terms would be small from one reaction to another. Actually the contributions of vibrations are important for these cases. Pitzer (37) carried through the calculations including all pertinent degrees of freedom; the reported discrepancy between theory and experiment then vanished.

In summary, it appears that there is not yet available a method whereby activation energies can be calculated in a satisfactory manner, but this is to

be interpreted as a shortcoming in physical models and mathematical techniques, not as a weakness in the general activated complex theory. The success of the theory in calculating absolute rates of reactions which have no activation energy and the calculation of  $A$ -factors for reactions, including those involving highly complex reactants, which do have activation energy, is strong confirmation of the general ideas involved. Many past claims of failure of the theory can be traced in some cases to inaccurate data and in others to the investigator's ignorance of molecular dynamics or unfortunate choice of approximations. For the future, theoretical kineticists should try to develop a widely applicable method of computation of activation energy, and also attention should be given to the development of a good "dynamic" method of calculation of reaction rates.

*Unimolecular reactions.*—The classical harmonic oscillator model of Slater (4) provides the most nearly satisfactory example of the dynamic method of calculating the rate of formation of the activated complex from the properties of the reactant molecule. Slater specifies the structure of the activated complex and the reaction coordinate; displacement along the reaction coordinate is given as a linear combination of normal modes of the reactant; and from an equilibrium distribution of energy over the independent normal modes, he has solved the formidable mathematical problem of computing the average rate with which the activated complex structure is assumed by the classically vibrating molecule. As Slater has emphasized, there are artificialities and shortcomings in this method; he has extended his work to the point that he has not one but many theories (43, 44). For example, consideration has been given to a small degree of anharmonicity, quantized oscillators, and the distribution of zeros, random or regular, over the trigonometric sum. Some of these theories are "dynamic," and some are essentially "structural." It is to be hoped that Slater will keep after the dynamic theory, examining the dynamic effects of quantized motions and anharmonicity in the normal mode coordinates as well as in the reaction coordinate. It is important to know how the activated complex is formed; in this sphere lies the unique advantage of Slater's work; a realistic qualitative (semiquantitative) picture of the process is more important at the present stage than the accuracy of the calculated rates.

For the high pressure case, Slater's method (4) and Eyring's method (3) are calculating the same rate, from one side and the other of microscopic reversibility. There is, however, an important difference in the physical model used: Slater's normal modes are independent, orthogonal coordinates, and his reaction coordinate is a dependent linear combination of normal modes; Eyring's reaction coordinate is independent and separable over a region  $\delta$ . As a consequence of these models, Slater's frequency factor is a molecular quantity, a weighted average of the frequencies of the normal modes contributing to the reaction coordinate, and Eyring's frequency factor is the universal quantity  $kT/h$ , valid for any separable single reaction coordinate. For cyclopropane the effect of this difference is small: Slater (4) carried through

a major computation, and found the value of  $A_\infty$  and the "fall-off" with pressure; by use of the method of Wilson & Johnston (35) for evaluating vibration frequencies of the bridged-hydrogen model and use of the structural method of the activated complex theory (note that Slater's degeneracy factor of 12 appears automatically as the ratio of symmetry numbers for the highly symmetrical reactant to the much less symmetrical complex), one can calculate a value of  $A$  in about 5 min. which is one-half as great as Slater's value and one-eighth the observed value. In Slater's completely specified, dynamic system, there is no room for the concept "entropy," and for this theory the factor of 4 discrepancy is very hard to bridge. By use of a different model with "looser" coordinates, the structural method can undoubtedly pick up a factor of 8 in the entropy term; however, it is one thing merely to give the discrepancy another name, "entropy," and it is another thing to show that a realistic activated complex structure has moments of inertia sufficiently increased and vibration frequencies sufficiently decreased to account for the observed discrepancy.

Because of the importance of cyclopropane as a test of Slater's theory, additional studies have been directed toward its mechanism. McNesby & Gordon (45) added deuterium to decomposing cyclopropane, found no HD, and concluded that if a biradical intermediate is formed, it isomerizes rapidly compared to free-radical attack on  $D_2$ . Lindquist & Rollefson (46) studied the rate of decomposition of cyclo- $C_3H_5T$ , but for this molecule, unlike cyclopropane itself, the symmetry is so low that the authors did not even try to interpret their data in terms of a vibrational analysis.

Pritchard (47, 48) has attacked the problem of high  $A$ -factors in unimolecular reactions for two sequences of decompositions, new data are given for these reactants, and the rate constants in  $\text{sec}^{-1}$  are (48): azomethane,  $1.5 \times 10^{14} \exp(-46.0/RT)$ ; hexafluoroazomethane,  $0.9 \times 10^{14} \exp(-48.5/RT)$ ; acetone,  $1.4 \times 10^{14} \exp(-70.9/RT)$ ; trifluoroacetone,  $0.3 \times 10^{14} \exp(-67.8/RT)$ ; trifluoroacetophenone,  $1.8 \times 10^{15} \exp(-73.8/RT)$ ; benzophenone,  $1.6 \times 10^{16} \exp(-87.5/RT)$ ; dibenzyl ketone,  $1.8 \times 10^{17} \exp(-71.8/RT)$ . The other series of reactions is for dialkyl mercury compounds with data from the literature. The proposal had been made that high frequency factors somehow arise if two modes of reaction happen to have about the same rate (49). Pritchard proposes that the two modes for the mercury dialkyls are the antisymmetric stretch which produces one alkyl radical and the symmetric stretch which produces two alkyl radicals with only slightly higher activation energy. The following equation from Fowler & Guggenheim (50) is taken to be the "general" expression for unimolecular reaction rates

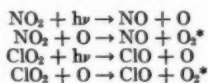
$$k = \lambda \exp(-E/RT) \sum_{r=1}^{\infty} (1/r!) (E/RT)^r \quad 2.$$

with  $\lambda$  interpreted as an average vibration frequency or about  $10^{13} \text{ sec}^{-1}$ . Equation 2 is certainly not the general expression for unimolecular reactions; it follows for the high pressure limit if and only if the specific dissociation

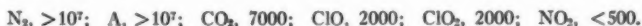
rate of an excited molecule is the same regardless of how much energy it has above the critical energy, that is, it is a pre-Rice-Ramsperger-Kassel (51) theory. Also in any case  $\lambda$  is not the vibration frequency  $10^{13} \text{ sec.}^{-1}$  but rather the vibration frequency divided by the average number of vibrations which the molecule undergoes between excitation and dissociation. Theory predicts (Slater or Kassel) and experiment confirms [ $\text{N}_2\text{O}$ ,  $2 \times 10^{10}$ ;  $\text{N}_2\text{O}_3$ ,  $1.4 \times 10^8$ ; cyclopropane,  $6 \times 10^7$ ; cyclobutane,  $3 \times 10^6 \text{ sec.}^{-1}$  (52)] that  $\lambda$  goes down as molecular complexity goes up, partially (or completely, according to Slater or Kassel) cancelling out the increase due to the summation term in equation 2 for  $A_\infty$ . At the low-pressure limit equation 2 has the correct form for classical harmonic oscillators, but  $\lambda$  is the second-order rate constant for deactivation. For the molecules discussed and the pressure range of their measurement, it is certain that one is not in the low pressure region of these reactions. Apparently this problem is not yet solved; although Pritchard is entirely correct in emphasizing that here a real problem exists.

*Energy transfer.*—The greatest stumbling block in the application of Slater's theory, structural activated complex theory, or any other theory to the region of "fall-off" of rate constant with pressure lies in a problem outside the range of these theories themselves, namely, the collision efficiency for deactivation of very highly excited polyatomic molecules. For vibrational-translational energy transfer, there probably are substantial differences in energy transfer rates between low-lying vibrational energy levels and the high levels just below the dissociation limit, and also there probably are substantial differences between diatomic and polyatomic molecules. Quantitative unimolecular reaction rate theory is at a standstill until one can solve the problem of collision efficiency for deactivation from, say, the twenty-fifth to the twenty-third vibrational energy level of a polyatomic molecule.

Lipscomb, Norrish & Thrush (53) produced oxygen molecules with up to 8 quanta of vibrational energy in the ground electronic state by flash photolysis of nitrogen dioxide or chlorine dioxide:



The excited molecules were observed by the usual flash-kinetic methods, and the rate of deactivation from the sixth vibrational level was measured as a function of the identity of foreign gas. The number of collisions to deactivate  $\text{O}_2^*$  from  $n=6$  to  $n<6$  was:



These results suggest that frequency resonance between the excited molecule and the foreign gas is important. The general picture is comparable to results obtained by sonic (54) methods for excitation and de-excitation of low lying vibrational levels.

Unimolecular decomposition rates in the low-pressure, second-order region give absolute rates of activation but only relative rates of deactivation from extremely high vibrational energy levels to levels not quite so high. The collision yield relative to the reactant itself for the decomposition of nitryl chloride at low pressures in a 50-liter bulb is as follows [Volpe & Johnston (55)]:

He	.15	H <sub>2</sub>	.15	CO <sub>2</sub>	.49
Ne	.22	N <sub>2</sub>	.34	N <sub>2</sub> O	.48
A	.30	O <sub>2</sub>	.34	SF <sub>6</sub>	.49
Kr	.36	Cl <sub>2</sub>	.50	SiF <sub>4</sub>	.51
Xe	.46	HCl	.63	CCl <sub>2</sub> F <sub>2</sub>	.71
				NO <sub>2</sub>	1.4

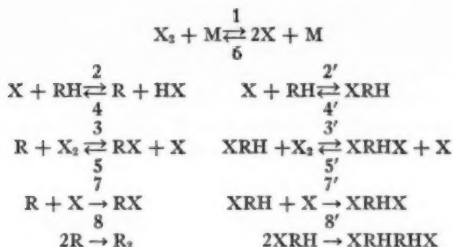
These results show no evidence of vibrational resonance energy transfer; instead they show excellent correlation with the boiling points of the foreign gases, and (excluding the dipolar gases) one finds direct proportionality with Lennard-Jones parameters in terms of collision force. The general picture is strongly unlike that at low or moderate energies as seen by sonic methods or shock waves. Even so, one can argue that the deactivation probability for all cases must be substantially below unity; the effect must be far from saturation for it to show direct proportionality to molecular parameters.

Bowen & Veljkovic (56) found that the fluorescence of perlene vapor is enhanced if a little vibrational energy is taken off. Efficiency of energy removal in this case, which has many parallels with the unimolecular reaction situation, was observed for nitrogen, *p*-cymene, naphthalene, and hexamethyl benzene. Data are presented graphically, not in tables; efficiency goes up, not without exception, with molecular weight, and thus with number of electrons, polarizability, boiling point, force of collision, etc.

#### MECHANISMS AND ELEMENTARY REACTIONS, QUANTITATIVE

For several complex systems, the authors have written down all elementary steps which are qualitatively normal or probable. they have assigned *A* and *E* factors of the Arrhenius equation either from the substantial list of observed values or from considerations of activated complex theory and bond energies, and from the long list of qualitatively reasonable steps only those are retained which are of dominant magnitudes. A rate expression was derived from the retained elementary steps, and the data fell right into the pattern predicted. Even if one or two steps have unknown rates, this procedure when applicable quickly solves the problem. A few mechanisms treated this way are discussed below, and a condensed list of a few especially interesting rate factors found this year will be given in the last part of this section.

*Halogenations.*—Goldfinger and associates (57, 58, 59) have given a complete account of the mechanisms of halogen substitutions, halogen addition, and dehydrohalogenation for chlorine and bromine and for an indefinitely large class of compounds which contain hydrogen. The mechanisms are



where the left-hand column refers to substitution and the right-hand column refers to addition reaction. In general it is shown that 5 and 5' are negligible. The general rate expression for either primed or unprimed mechanism is

$$\text{Rate} = \frac{(k_1[M])^{1/2}[\text{X}_2]^{1/2}}{(k_4[M]\alpha^2 + k_7\alpha + k_8)^{1/2}} \quad 3.$$

where  $\alpha$  is the ratio  $[\text{X}]/[\text{R}]$  and is given by  $(k_2[\text{X}_2] + k_4[\text{HX}])/k_3[\text{RH}]$ . From rough theoretical considerations, from dissociation energies, and from known rate factors, it is shown that chain termination may occur by way of any one of 6, 7, or 8, depending on reactants, temperature, and pressure. Depending on the termination reaction one gets substantially different rate expressions, orders, etc. Replacing  $k_1[\text{M}]$  by  $I_{\text{abs}}$  in equation 3, one obtains the corresponding rate for the photochemical reaction.

In the photochlorination of tetrachloroethylene (58), the Arrhenius plot showed a negative activation energy at low temperatures, a pronounced maximum at intermediate temperatures, and a positive activation energy at high temperatures, as termination shifts from 8 to 7 with increasing temperature and in accordance with predictions. The same activation energy,  $21 \pm 2$  kcal., was found for



in this system and in the photochemical dehydrochlorination of  $\text{C}_2\text{HCl}_4$  (59), and identical pre-exponential factor  $10^{11.5}$  cc. mole<sup>-1</sup> sec.<sup>-1</sup> for



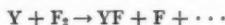
was found for each system.

The factors which determine the relative rates of 6, 7, or 8 are finely balanced; and depending on relative dissociation energies of  $\text{R}-\text{X}$  and  $\text{H}-\text{X}$ , temperature, and pressures, one finds one or another to predominate. From these considerations one sees the need for a broad range of conditions in the study of thermal or photochemical halogenations. The practice of combining photochemical data at one temperature with thermal data at another temperature without an adequate test for consistency of mechanism between the two cases leaves open the danger of operating under one rate law for one set of runs and another rate law for the other set of runs. It is

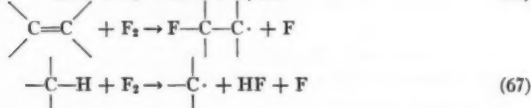


very probable that this is the explanation for the anomalous results on the bromination of neopentane and isobutane (35, 60, 61, 62).

The mechanisms for fluorination reactions are not yet on such firm grounds as those for bromination and chlorination, although novel and general features are appearing. In general the F—F bond is so weak compared to Y—F bonds (where Y is less electronegative than oxygen), that the reaction



is of general importance. Examples of this reaction and their reference number include



These rapid bimolecular reactions produce fluorine atoms much faster than the dissociation of the fluorine molecule. The fluorine atoms thus produced presumably follow Goldfinger's mechanism if hydrogen containing substances are involved, although steps 4, 5, 4', and 5' may be omitted because of energy considerations. If  $k_a'$  or  $k_a$  is the rate constant for the last two reactions above, the general rate expression is

$$Rate = \frac{k_a^{1/2} k_2 [F_2]^{3/2} [RH]^{1/2}}{(k_6 [M] \alpha^2 + k_{7\alpha} + k_a)^{1/2}} \quad 4.$$

where  $\alpha = [F]/[R] \approx k_3 [F_2] / k_2 [RH]$ . The three types of chain terminations lead to three different rate expressions; fluorination of hydrogen bromide (66) is given approximately by recombination by way of 6

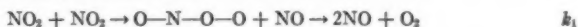
$$Rate = (k_a/k_6 [M])^{1/2} k_2 [F_2]^{1/2} [HBr]^{3/2} \quad 5.$$

*Other mechanisms.*—By calling on the common fund of rate factors for elementary reactions, Benson (68) gave a very satisfactory interpretation of the data on the thermal decomposition of methyl ether. An 11 step mechanism was written down, from quantitative considerations the mechanism was reduced to a much simpler one, and the derived rate expression agrees very well with data in the literature. For  $CH_3OCH_3 \rightarrow CH_3O + CH_3$  an activation energy of 81 kcal. was estimated.

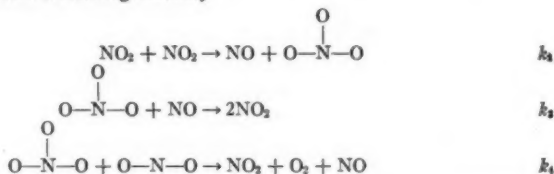
Another case where known rate factors for elementary reactions led to the mechanism, rather than the more usual converse, was the reaction between ethylene and deuterium and the decomposition of ethane in the presence of  $CD_4$  (69). The observed overall rate was entirely accounted for in terms of atom and free radical processes, and the authors conclude  $C_2H_4 + D_2 \rightarrow C_2H_4D_2$  and its reverse are unimportant elementary steps in their system.

Ayscough & Steacie (70) in one paper wrote down a complete and apparently definitive mechanism for the photolysis of hexafluoroacetone. They found an electronically excited molecule of appreciable lifetime; the primary process must go by way of production of  $\text{CF}_3$  and not by way of a reaction of the excited molecule; below  $200^\circ\text{C}$ . quantum yields are much less than one, presumably due to deactivation of the excited state with strongly different effects by different foreign gases; the radical  $\text{CF}_3\text{CO}$  decomposes rapidly at high temperature;  $\text{CF}_3$  does not abstract F or  $\text{CF}_3$  from hexafluoroacetone; no  $(\text{CF}_3\text{CO})_2$  is found; and there are no chain reactions. To clear up comparable problems with acetone required many years, many investigators, and the running down of many false leads.

Although examples are fewer, the oxides of nitrogen with oxygen atoms, molecules, and ozone illustrate almost as many principles of reaction kinetics as do all gas-phase organic reactions. These reactions form a family of their own with many elementary reactions appearing in more than one system. In addition to Bodenstein's reaction



for the thermal decomposition of nitrogen dioxide, Ashmore & Levitt (71) found another process occurring initially

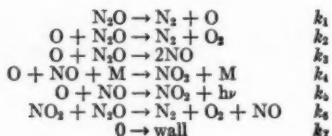


Reactions 1, 3, and 4 are well known (72) from older work. [Very significant recent results, involving direct spectroscopic observation of both  $\text{NO}_3$  and  $\text{NO}_2$ , have been discussed by Schott & Davidson (73) as a result of decomposition of nitrogen pentoxide in a shock tube.] At  $434^\circ\text{C}$ . Ashmore finds  $k_1 = 1.9 \times 10^3$ ,  $k_2 = 2.7 \times 10^3$  cc. mole $^{-1}$  sec. $^{-1}$ , and  $k_2/k_4 = 60$  with a fairly large error of estimate.

*Condensed quantitative data for elementary reactions.*—Newly discovered homogeneous unimolecular reactions which are probably elementary include:  $\text{Cl}_2\text{O}_7 \rightarrow \text{ClO}_4 + \text{ClO}_3$ ,  $k_{\infty} = 5.2 \times 10^{15} \exp(-33.5/RT)$  sec. $^{-1}$ , 100 to  $120^\circ\text{C}$ . (74); decomposition of cyclopentyl bromide,  $k = 8 \times 10^{11} \exp(-41.4/RT)$  sec. $^{-1}$ , 300 to  $350^\circ\text{C}$ . (75).

With a diffusion flame system at room temperature Garvin & McKinley (76) studied the emission from:  $\text{H} + \text{O}_3 \rightarrow \text{HO}^* + \text{O}_2$ ,  $k_1$ ;  $\text{HO}^* \rightarrow \text{HO} + h\nu$ ,  $k_2$ . If reaction 1 is rate determining,  $k_1 = 2.5 \times 10^{13}$  cc. mole $^{-1}$  sec. $^{-1}$ . If reaction 2 is rate determining, then reaction 1 occurs on every collision and the average life of the emitter is  $8 \times 10^{-8}$  sec. Klein *et al.* (7) report a constant of  $1.34 \times 10^{13}$  cc. $^2$  mole $^{-2}$  sec. $^{-1}$  for  $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$  at  $537^\circ\text{C}$ .

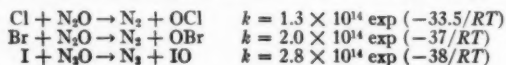
In a detailed and careful study of the initial rate and chemiluminescence in the thermal decomposition of nitrous oxide, Kaufman *et al.* (77) proposed:



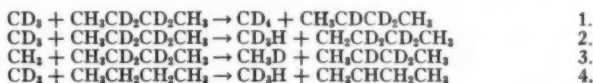
Experimental values found were:  $k_2 = 3 \times 10^{10} \exp(-14.5/RT)$  cc. mole<sup>-1</sup> sec.<sup>-1</sup>;  $k_3 = 10 \times 10^{10} \exp(-15.5/RT)$  cc. mole<sup>-1</sup> sec.<sup>-1</sup>;  $k_4 = 10^{18}$  cc.<sup>2</sup> mole<sup>-2</sup> sec.<sup>-1</sup>;  $k_5 \approx 10^6$  cc. mole<sup>-1</sup> sec.<sup>-1</sup> Pressman *et al.* observed reaction 5 under spectacular conditions, namely, release of nitric oxide from a rocket at 106 km. at night (78). By mercury photosensitized (at 2537 Å) decomposition of nitrous oxide, Cvetanovic (79, 80) has found the collision yields of oxygen atoms with a series of compounds: *cis*-butene-2,  $4.8 \times 10^{-3}$ ; *iso*-butene,  $5.9 \times 10^{-3}$ ; butene-1,  $1.4 \times 10^{-3}$ ; ethylene,  $2.2 \times 10^{-4}$ ; acetaldehyde,  $1.5 \times 10^{-4}$ ; *n*-butane,  $10^{-5}$  at 25°C. [See also (81).]

In addition to several current papers on the subject (82 to 86), Winkler and co-workers have written a review of active nitrogen (87) and a review of the reactions of nitrogen atoms (88). It is concluded that active nitrogen consists of nitrogen atoms and very highly excited vibrational states of recently formed diatomic molecules. The rate constant for  $\text{N} + \text{CH}_4 \rightarrow \text{HCN} + \text{H}_2 + \text{H}$  is given as  $10^{12} \exp(-13/RT)$  cc. mole<sup>-1</sup> sec.<sup>-1</sup>; and the reaction  $\text{N} + \text{CH}_3 \rightarrow \text{HCN} + 2\text{H}$  is said to be positively identified and extremely fast. Berkowitz, Chupka & Kistiakowsky (89) studied active nitrogen with a photomultiplier for light emission and with a mass spectrometer. A mechanism for the afterglow is given, and the rate constant for  $\text{N} + \text{N} + \text{N}_2 \rightarrow 2\text{N}_2$  was  $7 \times 10^{14}$  cc.<sup>2</sup> mole<sup>-2</sup> sec.<sup>-1</sup> where the probable error in the exponent is  $\pm 1$  and maximum error is  $\pm 2$ .

Dissociation of halogens and the recombination of halogen atoms have been studied at high temperature in shock tubes. Wray & Hornig (90) found a nominal value of 31 kcal. for the dissociation energy of fluorine; within experimental error this value is consistent with the accepted value of 36 to 37 kcal. and is inconsistent with any value above 38 kcal. Davidson and co-workers (91, 92) find the following values of rate constants:  $\text{Br} + \text{Br} + \text{A} \rightarrow \text{Br}_2 + \text{A}$ ,  $k = 3.4 \times 10^{14}$  cc.<sup>2</sup> mole<sup>-2</sup> sec.<sup>-1</sup> at 1600°K.;  $\text{I} + \text{I} + \text{A} \rightarrow \text{I}_2 + \text{A}$ ,  $k = 4.5 \times 10^{14}$  cc.<sup>2</sup> mole<sup>-2</sup> sec.<sup>-1</sup> at 1300°K. An interesting comparison for these high temperature rate constants is the corresponding data at room temperature, found by flash photolysis. Relative to argon, these rate constant ratios are: He, 0.36 at r.t., 0.5 at 1400°K.;  $\text{N}_2$ , 1.25 at r.t., 1.0 at 1300°K. if vibrationally unrelaxed, 1.6 at 1300°K. if vibrationally relaxed in the shock experiment;  $\text{O}_2$ , 1.8 at r.t., 1.2 at 1275°K.;  $\text{CO}_2$ , 3.7 at r.t., 1.6 at 1120°K.;  $\text{I}_2$ , about 300 at r.t., less than 30 around 1300°K. The authors discuss alternative explanations for these negative temperature coefficients. Kaufman *et al.* (93) studied bimolecular reactions of halogen atoms with nitrous oxide; around 927°K. rate constants in units of cc. mole<sup>-1</sup> sec.<sup>-1</sup> with energies as kcal. are:



One has the feeling that methyl radical reactions were the major battle of a few years ago; at the present the front of activity has moved on to  $\text{CH}_3$ ,  $\text{CF}_3$ , and higher alkane free radicals. Even so, considerable "mopping-up" activity is still occurring in this field. Of particular interest is the fact that Herzberg & Shoosmith (94) observed the absorption spectrum of  $\text{CH}_3$  and  $\text{CD}_3$  radicals between 1300 to 2200 Å. The radicals were produced by flash photolysis of mercury dimethyls, acetaldehyde, diazomethane, acetone, methyl bromide, and methyl iodide. The systematic determination of methyl affinities of olefins by Buckley & Szwarc (95) provides an interesting series. By direct mass spectrometric observation Ingold & Bryce (96) traced the rates and products of the reaction,  $\text{CH}_3 + \text{O}_2 \rightarrow ?$ , at 1000°C. The reaction was found to have a collision efficiency of  $10^{-4}$  to  $10^{-3}$ ;  $\text{CH}_3\text{O}_2$  was detected, but it quickly gives the secondary radicals  $\text{CH}_3\text{O}$ ,  $\text{HO}$ ,  $\text{HO}_2$ ,  $\text{CH}_2$ , and possibly  $\text{CHO}$ . McNesby *et al.* (97, 98) found the following data for  $\text{CH}_3$  and  $\text{CD}_3$  reactions:  $\text{CH}_3 + \text{D}_2 \rightarrow \text{CH}_3\text{D} + \text{D}$ , 140–450°C.,  $E = 11.9$ . The ratio of rate constant  $k_H$  for this reaction with  $\text{D}_2$  replaced by  $\text{H}_2$  by mass spectrometric ratios is:  $k_H/k_D = 9.2$  at 141°C., 2.9 at 424°C. For the series of reactions

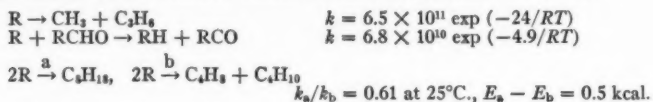


the rate constant ratios at various temperatures are:  $k_1/k_2 = 1.2?$  at 356°C., 1.0 at 401°C., 1.1 at 450°C.;  $k_1/k_2 = 1.08$  at 356°C., 1.06 at 401°C., 1.07 at 450°C.;  $A_2/A_4 = 1.50$ ;  $A_2/A_1 = 0.93$ ;  $E_{\text{primary}} - E_{\text{secondary}} = 2.1$  kcal. for  $\text{CD}_3$ .

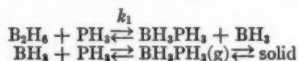
The  $\text{CF}_3$  radical is similar to the  $\text{CH}_3$  radical in its qualitative reactions, but it shows small interesting differences on a quantitative basis. To provide a test of some of the finer points of reaction rate theory, it is to be hoped that workers with this radical will persevere in their efforts until all reactants which have been studied with  $\text{CH}_3$  will also have been studied with  $\text{CF}_3$ . Investigations show photolysis of  $\text{CF}_3\text{NNCF}_3$  to be a very complicated system and a poor way to get quantitative data on  $\text{CF}_3$  reactions (99); photolysis of  $\text{CF}_3\text{COCH}_3$  and  $\text{C}_2\text{H}_5\text{COCF}_3$  is likewise a poor way to get  $\text{CF}_3$  (100); but on the other hand photolysis of  $\text{CF}_3\text{COCF}_3$  (70) is an excellent, clean, and highly recommended source of  $\text{CF}_3$ . In general  $\text{CF}_3$  abstraction of hydrogen has an activation energy 2 or 3 kcal. lower than the corresponding activation energy for  $\text{CH}_3$ , and the  $A$ -factors are of about the same order of magnitude (101). In anticipation of considerable activity in this field in the near future, these reactions are not abstracted in detail at present.

By photolysis of ketones and by addition of hydrogen atoms to olefins, various investigators have studied the reactions of ethyl and propyl (102), propyl (103), isopropyl (104), *n*-butyl (105), and *sec*-butyl (106). Typical findings are that these radicals (a) disproportionate, (b) combine, (c) abstract hydrogen from other molecules, or (d) decompose, above 350°C., to a hydrogen atom and an olefin. The bimolecular association for two like radicals has "steric factors" of 1,  $10^{-1}$ , 10 for methyl, ethyl, and propyl, respectively

(103). Here one notes the absence of a decreasing trend. For the secondary butyl radical, R, the relative values of various processes are (106):



An interestingly different sort of kinetic study was the reaction of di-borane with phosphine. Brumberger & Marcus (107) proposed



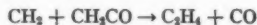
Between  $-24$  and  $0^\circ\text{C}$ .  $k_1 = 3 \times 10^9 \exp(-11.4/RT)$  cc. mole $^{-1}$  sec. $^{-1}$

#### MECHANISMS, QUALITATIVE

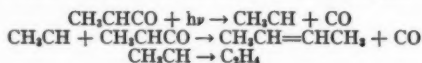
*Methylene free radicals.*—Interestingly enough, the  $\text{CH}_2$  radical is qualitatively different in its reactions from  $\text{CH}_3$  radicals, and the reactions are so fast that little quantitative information is available so far. It can be produced by photolysis of ketene,  $\text{CH}_2\text{CO}$ , or of diazomethane,  $\text{CH}_2\text{N}_2$ . In hydrocarbon solvents Doering *et al.* (108, 109) refer to methylene as an "indiscriminate reagent" and find that it adds to any and all carbon-hydrogen single bonds, to carbon-carbon double bonds, but that it does not add to carbon-carbon single bonds. Chanmugam & Burton (110, 111) believe  $\text{CH}_2$  adds to  $\text{H}_2$  in one step, and place an activation energy of 12 kcal. or more on



On the other hand, Gesser & Steacie (112) believe this reaction to be very fast, and they do not accept  $\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_4$ . Also Gesser & Steacie propose



as an important reaction. Kistiakowsky & Mahan (113) photolyzed methyl ketene at  $24^\circ\text{C}$ . From the products obtained, they propose



with the last two steps occurring at comparable rates. Holroyd & Noyes (114) photolyzed ketene in the presence of oxygen. Methylene adds to oxygen with a collision efficiency of about  $10^{-2}$ , followed by unidentified violent reactions of  $\text{CH}_2\text{O}_2$ . These authors were led to remark that  $\text{CH}_2$  is an extraordinarily reactive radical, not a quasistable molecule.

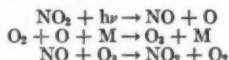
In the gas phase, Skell & Woodworth (115) produced *cis*-1,2 dimethyl cyclopropane from methylene and *cis*-2-butene. Kistiakowsky & Sauer (116) summarized the present status of methylene reactions:  $\text{CH}_2$  is an indiscriminate reagent in adding to double bonds and carbon-hydrogen single bonds both in the gas phase and in solution; however, the reaction is so exothermic that in the gas phase the product molecule breaks apart unless stabilized by

collision. In pure ketene,  $\text{CH}_2$  adds to  $\text{CH}_3\text{CO}$  to produce excited cyclopropanone, which, unless stabilized, splits with relative weight 2 to give  $\text{CH}_3\text{CH}_2\text{CO} \rightarrow \text{CH}_3\text{CH}_2 + \text{CO}$  or with relative weight one to give the diradical  $\text{CH}_2\text{COCH}_2$ . Older claims of relatively long lived radicals in flow systems refer to  $\text{CH}_2\text{COCH}_2$ , not  $\text{CH}_2$  itself.

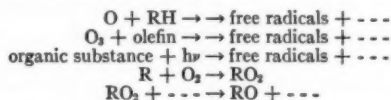
*High temperatures.*—A number of "classical" reactions were studied at high temperatures, relative to previous studies:  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ ,  $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$  (117);  $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$  (118);  $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$  (119). In general, these data are consistent with low temperature results, although slight changes of mechanism would not have been detected by the methods used. There is considerable interest in high temperature processes (120). With studies of fast reactions, one often considers the possibility that at sufficiently high temperatures and high rates, the distribution of excited reactants will be so distorted that calculations made by the usual theories will be of no use. The "fall-off" of rates of elementary unimolecular reactions from this effect is fairly well understood, as well as its dependence on temperature and pressure. There are good reasons to believe such effects are negligible for elementary bimolecular reactions. However, much worse complications are expected at very high temperatures: the reactants of bimolecular reactions may decompose unimolecularly, elementary processes may become chain processes, chain processes may change their mechanism, the hot products of exothermic reactions may activate reactants with energy transfer becoming rate determining, etc. Big effects are to be sought not in a change in the theoretical expressions for the rate constant of an elementary reaction, but rather in qualitative changes in the mechanism.

*Smog.*—In the oil "smog" or atmospheric pollution often found in the Los Angeles basin, there is reduced visibility, a bad odor, eye irritation, respiratory irritation, rubber cracking, plant damage, etc., with peak values at midday and only residual effects at night. Several years ago Haagen-Smit (121, 122 and references cited therein) proposed a qualitative mechanism, which, corrected for certain quantitative rates in the oxide of nitrogen system (123, 124), has recently received confirmation from a variety of sources (125 to 128). At present the mechanism appears to be:

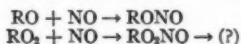
#### I. Inorganic photochemical cycle



#### II. Organic free radical chain oxidation



#### III. Effect of organic radicals on inorganic cycle



Ozone produces the rubber cracking, but most other toxic effects are presumably due to the partially oxidized molecular and free radical (129) intermediates, such as the peroxyxynitrites, etc. Nitric oxide strongly suppresses ozone (124), and it must be removed for ozone to build up. The overall process is the nitrogen dioxide sensitized photochemical oxidation of organic vapors. Ozone is a byproduct and indicator: when ozone is high, nitric oxide is low, because organic free radicals are high due to the rapid occurrence of photochemical combustion with poisonous intermediates.

*Sodium atoms.*—Riding, Scanlan & Warhurst (130) studied the rate of reaction of sodium atoms with 31 different aromatic halides by the diffusion flame technique. The original simplest method of calculating data was employed. Results are not in good agreement with other workers in this field (factor of 2 to 4) nor with a different technique (factor of 7). The authors believe relative values over the series are significant, and they discuss trends with ortho, meta, and parasubstitution. Cvetanovic (131) has completed extensive computations on this experimental method and has published useful graphs and tables.

*Individual systems of an unusual nature.*—Toby & Schiff (132) produced D atoms on a hot tungsten filament and mixed them with ethylene. The distribution of D in the products was surprising: the most abundant ethanes were  $C_2H_6$  and  $C_2H_5D$  while the methanes were highly deuterated.

A preliminary study of the photolysis of pentaborane at 2050 Å indicates production of a hydrogen atom as the primary step [Burwasser & Pease (133)].

Stewart & Cady (134) studied the thermal decomposition of the highly unstable perfluoroacetic acid,  $CF_3COOF$ , into the extremely stable products,  $CF_4$  and  $CO_2$ . The initial step is believed to be a breaking of the O—F bond (25 kcal.) followed by a splitting to  $CF_3$  and  $CO_2$  and long chains carried by  $CF_3$  abstraction of F from the carboxyl group. This scholarly investigation was enlivened by a number of violent detonations.

*Other reviews.*—The appearance during the year of a review article on some specialized topic is an adequate reason for not reviewing that topic here. The subject of the primary photochemical processes in simple ketones was reviewed by Noyes, Porter & Jolley (135). Norrish & Thrush (136) presented a review of flash photolysis and kinetic spectroscopy. Gray (137) reviewed reactions of nitrogen dioxide with free radicals. Reviews of active nitrogen have been mentioned (87, 88).

#### EXPERIMENTAL METHODS

Kistiakowsky & Kydd (138) reported an x-ray absorption spectrometer for following the density of gas in a shock tube for the study of detonation wave forms. Bair, Lund & Cross (139) have developed a method which in part overcomes the usual dilemma between speed and precision in the study of reaction rates. They submit their system to periodic pulses, an electric discharge in this case, followed by an observation at a known time later. An electronic accumulator integrates the effect of a large number of pulses,



thereby increasing the precision of the observation. Preliminary results on  $\text{NH}_2$  produced from ammonia show considerable promise of high precision rates at the millisecond time scale.

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# KINETICS OF REACTIONS IN SOLUTION<sup>1</sup>

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This review deals with homogeneous reactions in liquid solution; studies in the areas of photochemistry, radiation chemistry, and polymerization kinetics are not reviewed. A short review of the past year's work in enzyme kinetics is included, and this inclusion has necessitated a somewhat abbreviated review of organic reactions. In a sense, the entire review is abbreviated since fewer than half of the worth-while papers published during the year are included.

A short book by Dainton (1) on chain reactions, including those in solutions, has appeared during the year as have reviews of the kinetic studies published in 1955 [Noyes (2); Ashmore *et al.* (3)]. Guggenheim (4) sets the record straight on the early history of kinetics and points out that the lack of correlation between the reaction order and the coefficients in the chemical equation was realized by the earliest workers in the field. If the teacher wishes to emphasize this point, a nice example is the reaction,  $30 \text{ ROH} + \text{B}_{10}\text{H}_{14} \rightarrow 10 \text{ B(OR)}_3 + 22 \text{ H}_2$ , which Beachell (5) finds to be first order in ROH and in  $\text{B}_{10}\text{H}_{14}$ .

The design of a four-channel stop flow mixing apparatus for use with the Beckman D.U. spectrophotometer is presented by Beers (6), and De Tar (7) describes apparatus for the precise manometric determination of rate data. Under the heading of neat tricks is Winstein's use of a tape recorder for noting the time of quenching of reaction mixture aliquots (8); this technique should prove useful for the solitary researcher who is studying a relatively rapid reaction.

Westman & De Lury (9) have considered the integrated rate equations for consecutive first order reactions, and Widequist (10) describes a method for the calculation of the rate constants for two competitive, consecutive reactions; this method is applicable to experiments in which the reactants are present in nonequivalent amounts.

Harris & Weale (11) have measured the rates of several reactions as a function of pressure up to pressures of 5000 atm. The value of  $\Delta V^\ddagger$  is often dramatically different at high pressures from what it is at one atmosphere, a point also stressed by Hamann (12).

Noyes (13) has presented theoretical considerations pertaining to diffusion controlled reactions and concludes that current data suggest "that diffusion in liquids involves almost continuous motion and small individual displacements, and does not involve 'jumps' of the order of a molecular diameter that are opposed by significant potential barriers." Other theoretical papers dealing with diffusion controlled reactions are by Schulz (14) and

<sup>1</sup> The survey of literature pertaining to this review was completed in December, 1956.

Monchick (15). Hamill & Williams (16) have continued experimental studies which have relevance in this area.

#### INORGANIC REACTIONS

*Oxidation-reduction reactions.*—The action of hydrogen as a reducing agent in homogeneous solution has been reviewed by Weller (17), Halpern (18) and Winfield (19). Wilmarth finds the rate of reduction of copper (II) acetate in quinoline to be proportional to  $(H_2)(CuAc)_2^2$ ; this autocatalytic reaction, with  $\Delta H^\ddagger = 13$  kcal., proceeds more slowly with deuterium (20). The hydrogen reduction of silver acetate in pyridine is first order in silver (I) [Wilmarth (21)]. For the  $Cu^{++}$ -catalyzed reduction of  $Cr^{VI}$  by  $H_2$ , Halpern finds,  $Rate = k(Cu^{++})^2 (H_2)/[(Cu^{++}) + k' (H^+)]$  which indicates an intermediate  $CuH^+$  is produced in the first step of the reaction; the following step,  $CuH^+ + Cu^{++} \rightarrow 2 Cu^+ + H^+$ , produces the species which rapidly reduces  $Cr^{VI}$  or some other substrate (22). Copper (II) complexes (23) and silver (I) (24) also catalyze this reaction. The rate of hydrogen reduction of  $Hg_2^{++}$  and  $Hg^{++}$  in the presence and absence of complexing anions has been studied by Halpern (25).

No simple generalizations can be made regarding the kinetics of oxidation of metal ions by oxygen. An abnormally high frequency factor and a sensitivity to catalytic and inhibitory effects suggest to Halpern (26) that the  $O_2$ — $U^{IV}$  reaction proceeds by a chain mechanism. The  $O_2$ — $Pu^{III}$  reaction is second order in  $Pu^{III}$  [Newton (27)], while the  $O_2$ — $Fe^{II}$  reaction shows both first and second order dependence upon  $Fe^{II}$  [Davidson (28)]. The catalytic influence of anions upon the  $O_2$ — $Fe^{II}$  reaction parallels the stability of the corresponding complexes of  $Fe^{III}$ , thus supporting the transition state geometry  $[X-Fe-O_2]^{\ddagger}$  suggested by Weiss (29). Abel (30) suggests a different role of anions in oxygen reactions and also presents discussions of the  $O_2$ — $Cu^I$  reaction, the  $Cu^{II}$  catalysis of the  $O_2$ -ascorbic acid reaction and the reactions in the peroxide-iron system (31).

Closely related to the  $O_2$  reactions are those involving peroxides; several kinetic studies of inorganic peroxide reactions have appeared during this year. Ball & Edwards (32) find the decomposition of  $H_2SO_5$  to proceed via a transition state  $HSO_5SO_5^{-2}$ . The rate of formation of both  $H_2SO_5$  and  $HCO(OOH)$ , studied by Redlich (33), can be measured only in very concentrated solutions, and thus uncertainty regarding medium effects renders the interpretation of the rate data difficult. The  $Ag^I$ -catalyzed oxidation of  $Ce^{III}$  by  $S_2O_8^{2-}$  has been investigated by Fronaeus (34), and studies have been made on the rate of decomposition of peroxy species of  $U^{VI}$  (35) and  $Ce^{IV}$  (36).

Kinetic studies on metal ion-metal ion reactions published during the year reveal uncomplicated second order kinetics for some systems and complexities in others. The  $Co^{III}$ — $Ce^{III}$  reaction proceeds via a transition state  $CeCoOH^{+4}$  which suggests an hydroxyl bridge structure [Sutcliffe (37)]; since this transition state has a charge of +5, it is not surprising that the

reaction rate increases with an increase in the total anion concentration at constant  $\mu$ . The relatively rapid second order reaction of  $\text{Pu}^{+3}$  and  $\text{PuO}_2^{++}$  has been studied by Rabideau (38). The unusual influence of  $\text{Cl}^-$  upon the rate of the  $\text{Fe}^{\text{II}}-\text{Ti}^{\text{III}}$  reaction observed by Duke (39) is reminiscent of its effect on the  $\text{Ti}^{\text{I}}-\text{Ti}^{\text{III}}$  exchange (40). The value of the second order rate constant for the  $\text{Sn}^{\text{II}}-\text{Ce}^{\text{IV}}$  reaction in sulfuric acid solutions is independent of the ionic strength [Brubaker (41)]. The rate of the reaction of  $\text{Cr}^{\text{VI}}$  and  $\text{As}^{\text{III}}$  has been studied by Kolthoff (42) who also elucidates the reduction of  $\text{O}_2$  induced by this reaction. Sutcliffe (43) has studied the rates of certain metal ion oxidation-reduction reactions in glacial acetic acid. The retarding effect of a product may reveal the formation of an unstable intermediate in a reaction step preceding the rate-determining step. Thus  $\text{Ti}^{\text{II}}$  is shown to be an intermediate in the  $\text{Co}^{\text{III}}-\text{Ti}^{\text{I}}$  reaction by the retarding effect of  $\text{Co}^{\text{II}}$  [Ashurst & Higginson (44)], and  $\text{Hg}^\circ$  is shown to be an intermediate in the  $\text{Ti}^{\text{III}}-\text{Hg}^{\text{I}}$  reaction by the retarding effect of  $\text{Hg}^{\text{II}}$  [Armstrong, Halpern & Higginson (45)].

Studies of the rate of oxidation of organic reducing agents by metal ions include the  $\text{Fe}^{\text{III}}-\text{HSCH}_2\text{COOH}$  reaction [Leussing (46)], the  $\text{Ti}^{\text{III}}-\text{HCOOH}$  reaction [Halpern (47)], the  $\text{Ce}^{\text{IV}}-\text{C}_2\text{H}_5\text{OH}$  reaction [Ardon & Stein (48)], and the  $\text{Mn}^{\text{III}}$  pyrophosphate and  $\text{Pb}^{\text{IV}}$  acetate oxidation of 1:2 glycols [Waters (49)]. The  $\text{Ti}^{\text{III}}$  reduction of certain azo compounds in  $\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}$  solution shows a complicated dependence upon  $(\text{HCl})$  [Hinshelwood (50)].

The kinetics of oxidation-reduction reactions involving oxyanions have been the subject of a number of papers including a brief review by Taube (51). The rapid oxidation of sulfite by  $\text{I}_2$  has been studied by Eigen (52); under limiting conditions (high  $(\text{I}_2)$ ), the hydration of  $\text{SO}_2$  becomes rate-determining ( $t_{1/2} \approx 10^{-3}$  sec.). For the nitrite-sulfite reaction, Seel finds the rate law

$$\frac{d(\text{HON}(\text{SO}_3)_2^-)}{dt} = k_1(\text{H}^+)^2(\text{NO}_2^-) + k_2(\text{H}^+)^2(\text{NO}_2^-)(\text{SO}_3^-)$$

with a value of  $k_1$  in agreement with other observations of the rate of production of  $\text{NO}^+$  (53). The reaction of  $\text{ON}(\text{SO}_3)_2^-$  and  $\text{HON}(\text{H})\text{SO}_3^-$  to yield this same product  $\text{HON}(\text{SO}_3)_2^-$  is catalyzed by the  $\text{Fe}^{\text{II}}-\text{Fe}^{\text{III}}$  couple [Yost (54)]. Other reactions of oxyanions which have been the subject of kinetic studies are the  $\text{BrO}_3^- - \text{Cl}^-$  reaction (55), the decomposition of  $\text{OCl}^-$  and its reaction with  $\text{OCN}^-$  (56), the  $\text{HNO}_2-\text{H}_2\text{C}_2\text{O}_4$  reaction (57), the  $\text{S}_2\text{O}_8^{2-}$ -hydrazobenzene reaction (58), the  $\text{Br}_2-\text{HCOOH}$  reaction (59) and the  $\text{MnO}_4^- - \text{HCOOH}$  reaction (60, 61, 62).

Information regarding the kinetic salt effect has been the primary objective of two oxidation-reduction reaction studies. Baxendale (63) finds the second order rate constant for the  $\text{Fe}^{++}-\text{Co}(\text{C}_2\text{O}_4)_2^{2-}$  reaction to vary with  $\mu$  at  $\mu \leq 4 \times 10^{-3}$  in accordance with the Brönsted-Debye-Hückel equation; the generalization  $\Delta S^\ddagger = -10Z_A Z_B$  e.u., which is found in many textbooks,



predicts a values of  $\Delta S^\ddagger$  different by over 60 e.u. from that observed. The kinetic salt effect of NaCl, at concentrations as high as 4*M*, upon the  $S_2O_8^{2-}-I^-$  reaction has been studied by Schwab (64).

*Exchange reactions.*—McConnell (65) evaluates the second order rate constant for  $Cu^I-Cu^{II}$  exchange in 12 *M* HCl to be  $0.5 \times 10^8$  l. mole<sup>-1</sup> sec.<sup>-1</sup> from the influence which the paramagnetic  $Cu^{II}$  ion ( $10^{-4}$  to  $10^{-2}$  *M*) exerts upon the  $Cu^{63}$  nuclear resonance line width for 1 *M* CuCl. Since this rate constant corresponds to a half time of  $1.4 \times 10^{-5}$  sec. at  $10^{-3}$  *M* copper, it is clear that this new technique extends considerably the exchange rates accessible to measurement. An upper limit of  $4 \times 10^8$  l. mole<sup>-1</sup> sec.<sup>-1</sup> for the rate constant for the  $W(CN)_8^{4-}-W(CN)_8^{3-}$  exchange has been established by the influence of  $W(CN)_8^{4-}$  on the paramagnetic resonance absorption of  $W(CN)_8^{3-}$  [Weissman & Garner (66)]. An activation energy of  $1840 \pm 250$  cal. for the proton transfer process between  $H_3O^+$  and HF in moist liquid HF has been deduced from the temperature dependence of nuclear magnetic relaxation times [Soloman & Bloembergen (67)].

The rapid exchange of  $Pu^{III}$  and  $Pu^{IV}$  has been studied by conventional means by Keenan (68), who finds that  $OH^-$  is incorporated into the transition state. Duke (69) finds that only transition states containing  $OH^-$  are important for the  $Ce^{III}-Ce^{IV}$  exchange reaction even at 5 *M*  $HClO_4$ ; two reaction paths, one involving one  $Ce^{III}$  and two  $Ce^{IV}$  atoms and one involving one  $Ce^{III}$  and one  $Ce^{IV}$  atom, accomplish the exchange. An exchange reaction path with a rate-determining step involving zero  $Ce^{IV}$  atoms suggested by the earlier work of Dodson (70) is not confirmed.

Studies of neptunium exchange reactions have been continued by Hindman and coworkers. They find the rate of exchange of  $NpO_2^+$  and  $NpO_2^{++}$  in  $H_2O$ -glycol and  $H_2O$ -sucrose solutions does not vary appreciably with a change of dielectric constant ( $D=68-88$ ); since the value of  $\Delta Z_{act}^2$  is +4 if  $ClO_4^-$  is not a part of the transition state, simple reasoning on the basis of electrostatic considerations does not rationalize this result (71). The rate of exchange of  $Np^{IV}$  and  $Np^{VI}$  in  $H_2O$ -glycol solutions (0–12 *M* glycol) goes through a maximum at  $\sim 6$  *M* glycol (72).

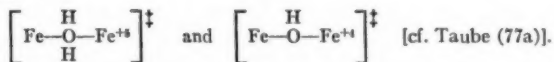
Antimony exchange studies have been carried out by several workers. The rate law,

$$\text{Rate} = k_1(SbCl_5) + k_2(SbCl_5)(SbCl_5)^2$$

has been found by Kahn (73) for the exchange reaction in  $CCl_4$  solutions. The behavior in aqueous solution is complicated by the inertness of  $Sb^V$  species. Neumann (74) finds that  $SbCl_6^-$  is the reactive form of  $Sb^V$ ; this species forms slowly in 6 *M* HCl. The hydrolysis rate for  $SbCl_6^-$  has been measured in media with 6 *M*  $Cl^-$  and 9 *M*  $Cl^-$ ; in both media, transition states involving zero and one hydrogen ions are important and catalysis of the hydrolysis by  $Sb^{III}$  is also observed [Neumann (75)]. Bromide ion catalysis of the exchange reaction has been observed by Turco & Faraone (76).

The rate constants for the two paths for the  $Fe^{II}-Fe^{III}$  exchange,  $Fe^{++}$

$+Fe^{+++} \rightarrow$  and  $Fe^{++} + FeOH^{++} \rightarrow$ , are twofold lower in heavy water than in ordinary water [Dodson (77)]. Since it is only the transition state containing hydroxide ion which can have a symmetrical structure for hydrogen atom transfer, perhaps these data suggest oxygen bridged transition states for both paths:



The rate of exchange of oxygen between  $\text{BrO}_3^-$  and water has been found to occur via a transition state of the composition  $\text{H}_2\text{BrO}_3^+$ ; in this study, Hoering finds the rate to be 1.7 fold larger in  $\text{D}_2\text{O}$  than in  $\text{H}_2\text{O}$  (78).

The study of the exchange of sulfur between  $\text{RS}_2\text{O}_3^-$  and  $\text{SO}_3^-$  by Fava (79) includes an investigation of the influence of several electrolytes upon the rate. The exchange of cobalt between the ethylenediamine-tetraacetate complexes of  $\text{Co}^{\text{II}}$  and  $\text{Co}^{\text{III}}$  has been studied by Adamson (80). The x-ray induced exchange of  $\text{Tl}^{\text{I}}$  and  $\text{Tl}^{\text{III}}$  has been studied by Challenger & Masters (81) who with Luehr derive equations for the course of an exchange reaction which accompanies a net chemical change (82). Another paper dealing with mathematical aspects of exchange reactions is that by Harris (83).

*Substitution reactions in inert octahedral complexes.*—In contrast to the low rate of most substitution reactions involving  $\text{Co}^{\text{III}}$  and  $\text{Cr}^{\text{III}}$ , the rate of formation of certain nitritocobalt (III) amines from the corresponding aquoamine in weakly acidic solution is high. Murmann & Taube (84) have shown this reaction to occur without rupture of the  $\text{Co}-\text{O}$  bond, and the isomerization to yield the nitro complex occurs by an intramolecular path; the rate of this transformation for *cis* and *trans*  $\text{Co}(\text{en})_2(\text{ONO})_2^+$  has been studied by Adell (85). The rates of base-catalyzed hydrolysis of certain halo-cobalt amines have been studied by Pearson & Basolo (86), who use a conductivity flow apparatus for the rapid reactions, and by Ingold, Nyholm *et al.* (87), who focus attention on the stereochemistry of the reactions. The former workers consider that such second order reactions proceed via the unimolecular reaction of the conjugate base of the complex ion while the latter workers favor an  $\text{S}_{\text{N}}2$  interpretation. The stabilization by  $\pi$  bonding of the pentacoordinated species which would result from the unimolecular loss of halide ion has been discussed by Pearson & Basolo (88). It is interesting that the rate of aquation of  $\text{Co}(\text{en})_2\text{F}_2^+$  is proportional to  $(\text{H}^+)$  at  $(\text{H}^+) > 10^{-2} M$  in contrast to the  $(\text{H}^+)$ -independence of the aquation rate of the analogous chloro- and bromo-complexes [Basolo (89)].

Additional publications dealing with kinetics of complex ion reactions are the studies of the formation of a polymeric  $\text{Cr}^{\text{III}}$ -oxalate species (90), the dissociation of tris (2,2' dipyridyl)-iron (II) (91), the displacement reactions of metal ethylenediaminetetraacetate complexes (92) and the formation of a  $\text{Ni}^{\text{II}}$ -orthophenanthroline complex (93).

*Miscellaneous inorganic reactions.*—The thermal decomposition of liquid  $\text{HNO}_3$  slows down dramatically as reaction occurs suggesting that  $\text{N}_2\text{O}_5$  is

the reactant in the rate-determining step (94). The rate of decomposition of  $O_3$  in 0.01 *M*  $HClO_4$  is found by Kilpatrick (95) to be proportional to the 1.5 power of  $(O_3)$ , lending support to the chain mechanism suggested by Weiss. The use of thioacetamide in sulfide precipitation procedures in inorganic qualitative analysis has stimulated an interest in its rate of hydrolysis (to yield  $H_2S$ ). Swift (96) has found this rate to be proportional to  $(H^+)$  but finds the mechanism of formation of  $PbS$  at  $pH=3.5-5.1$  does not involve the intermediate formation of  $H_2S$ . Roughton's thermal method for studying fast reactions applied to the reaction  $CO_2 + OH^- \rightarrow HCO_3^-$  yields the constant  $k = 4.2 \times 10^{13} \text{ mole}^{-1} \text{ l. sec.}^{-1} \exp(-13,250/RT)$  [Pinsent (97)]; a more precise calculation of the rate of the reaction  $CO_2 + H_2O \rightarrow H_2CO_3$  from existing data gives the interesting result that  $\Delta C_p^\ddagger \cong -220 \text{ cal. deg.}^{-1}$ . These same authors have also measured the rate of reaction of  $CO_2$  with  $NH_3$  (98). The reaction  $8(C_6H_5)_3P + S_8 \rightarrow 8(C_6H_5)_3PS$  is second order and shows great sensitivity to solvent [Bartlett (99)]. The rate of decomposition of cyanate has been studied in alkaline solution by Kemp & Kohnstam (100) and in acidic solution by Amell (101).

#### ORGANIC REACTIONS

*Acid-base catalysis.*—Kinetic studies on eight reactions using  $HF$  as an acid catalyst have been made by Bell (102); for each of the reactions subject to general acid (or base) catalysis, the catalytic constants for  $HF$  (or  $F^-$ ) correlate with a Brönsted equation using parameters appropriate to the carboxylic acids (or carboxylate ions). This result, surprising in view of the different contributions of resonance stabilization of the anion to the acid strength of these two types of acids, is rationalized in terms of the bond strength of the  $H-F$  bond. Bell uses his thermal maximum method in a study of the hydration of acetaldehyde, for which the catalytic constants of bases fail to obey the Brönsted relationship (103), and in measuring the rate of neutralization of nitroethane by metallic hydroxides, which leads to values of the dissociation constants of  $CaOH^+$ ,  $BaOH^+$  and  $TiOH$  (104). Kinetic studies on acid catalysis in aprotic solvents include the isomerization reactions of  $5\alpha$ ,  $6\beta$  dibromocholestane in  $C_6H_6$  [Kwart (105)] and 1—phenylallylchloride in  $C_6H_5Cl$  [Braude (106)] and the dimerization of certain diaryl ethylenes in  $C_6H_6$  [Evans (107)]. Solvolysis studies on alkyl borates in alcohol reveal both general acid and base catalysis [Crowell (108)], while the solvolysis of benzaniline in  $MeOH-H_2O$  shows a complex dependence upon  $(H^+)$  [Willi (109)]. The rates of the acid-catalyzed hydrolysis of certain cyclic 1:2 sulfitess have been measured by Bunton (110), who also demonstrates by the use of  $O^{18}$  that it is the  $S-O$  bond which breaks.

Complicated empirical rate laws are often required for acid- or base-catalyzed reactions in which a reactant acid or base is also the only source of the catalyst; such is the situation in studies of the acid-catalyzed maleic acid-fumaric acid transformation [Davies (111)] and the base-catalyzed ethyl formate—butylamine reaction [Watanabe (112)].

A correlation of the reaction rate and the Hammett acidity function,  $H_0$ , provides the interesting information that the transition state has the composition  $SH^+$  and not  $SH_3O^+$  if the assumption that  $y_S/y_{SH^+} = y_B/y_{BH^+}$  is valid. Mild variations of the value of  $-d \log k/dH_0$  from 1.0 are generally interpreted to mean that this assumption is not strictly valid. The values 1.2 and 1.25 have been observed for the hydrolysis of methyl mesitoate in  $HClO_4$  and  $H_2SO_4$  solutions, respectively; rate data on other substituted benzoate esters show the correlation  $rate \propto (H_3O^+)$  indicating the transition state is  $SH_3O^+$  [Long (113)]. A correlation of the rate of hydrolysis of peracetic acid with  $(H_3O^+)$  in aqueous perchloric acid has been observed by Bunton (114). The depolymerization of trioxane in concentrated aqueous HF exhibits the dependence  $-d \log k/dH_0 = 1.2$ ; it is interesting to note that  $H_0 = -2.1$  at 42.7 per cent HF, an unexpected value for a weak acid. Bell (115) explains this in terms of the reaction,  $nHF \rightleftharpoons H^+ + H_{n-1}F_n^-$ , which leads to an abnormally high value of  $d \log (H^+)/d \log C_{HF}$  for  $n \geq 2$ . Values of  $-d \log k/dH_0$  ranging from 0.86 to 1.06 for the hydrolysis of ethylene oxide derivatives in aqueous perchloric acid have been observed by Pritchard & Long (116). Additional studies in which a correlation between reaction rate and  $H_0$  have been observed include two reactions involving protonated formaldehyde (117), the ethanolysis of certain esters to yield olefins (118), the hydrogen exchange between anisole and acidic media (119), and the formation of the sulfate ester of 2,4-dinitrobenzyl alcohol in concentrated  $H_2SO_4$  (120).

Kreevoy (121) finds the first order rate constants for the hydrolysis of certain acetals and ketals in moderately concentrated perchloric acid solutions in 50 per cent dioxane to be given by

$$\log k_1 = \log (HClO_4) + 0.864 (HClO_4) + \text{const.},$$

a relationship which is also valid for  $\log \{(BH^+)/(B)\}$ . Deno (122) correlates the rate of aromatic nitration in concentrated  $H_2SO_4$  with the  $C_0$  acidity function  $\{C_0 = pK_R + \log (ROH)/(R^+)\}$ , and Gold (123) discusses the dependence of aromatic sulfonation upon acidity in concentrated  $H_2SO_4$ .

Schubert (124) has carried out kinetic studies on the decarbonylation of aromatic aldehydes in concentrated  $H_2SO_4$  and  $D_2SO_4$ ; isotope effect variation with the concentration of the acid, combined with previously reported dependence of the rate upon  $(H_2SO_4)$ , suggest a mechanism consisting of two steps, each a proton transfer.

*Solvolysis and displacement reactions.*—The comprehensive review on "Solvolytic Displacement Reactions at Saturated Carbon Atoms" by Streitwieser has appeared during the year (125); with over 760 references and much interpretive comment, this paper is an invaluable addition to the literature.

For solvolytic reactions carried out in dilute solution in the solvent with which the substrate (RX) is reacting, the order of the reaction with respect to solvent is kinetically inaccessible; the classifications  $S_N1$  and  $S_N2$  are never-

theless widely used in such cases although the specific participation of zero and one solvent molecules in the transition states cannot be considered proved. Recently there has been considerable discussion of a concept of border-line mechanisms which are intermediate between these two extremes (but not the concurrent independent operation of the two); different authors may very well have different things in mind when discussing the concept. Gold (126) effectively criticizes this concept by pointing out that a particular transition state must contain an integral number of molecules. While this is true, the uncertainty in defining, let alone measuring, the specific solvation of stable solute species makes it clear that the problem is not an easy one when concerned with transition states. In connection with work on the hydrolysis of acid chlorides, Hudson (127) adheres to the point of view that the two paths operate concurrently, while Hyne & Robertson (128) consider the border-line mechanism concept a fruitful one and discuss the solvolysis of benzenesulfonic esters in various pure and mixed solvents in such terms; the observed correlation of the  $E_A$  values for these solvolysis reactions with empirical equations involving the molar volume and dielectric constant of the solvent does not seem particularly relevant to the question of the alleged border-line nature of the reaction mechanisms.

The  $E_A$  values for the base-catalyzed hydrolysis of phenyl methanesulfonate and phenyl *p*-toluenesulfonate are very similar to the values observed for certain alkyl sulfonates despite the fact that it is the S—O bond being broken in the phenyl compounds [Bunton (129)]. Values of  $\Delta C_p^\ddagger = -30$  to  $-70$  cal./deg. have been observed by Kohnstam (130) in a study of the solvolysis of some phenylchloromethanes.

From measurements of the rate of solvolysis of *t*-butyl chloride in a number of 2-component solvents, Fainberg & Winstein (8) have greatly extended the solvent composition ranges for which the "ionizing power,"  $Y$ , is known. ( $Y = \log k/k_0$ , where  $k_0$  is the rate constant for the *t*-butyl chloride solvolysis in 80% EtOH). Parameters for the least square fit of the values of  $Y$  to a quartic equation for each solvent pair are presented. The correlation of solvolysis rates with  $Y$  is remarkably good if a different  $m$  value is used for a particular compound in each solvent pair. On the other hand, correlations of the value of  $\log k$  for the solvolysis of *t*-butyl chloride with  $\{(D-1)/(2D+1)\}$ , a function with theoretical significance, show much dispersion. It is interesting that the spectral transition energies for the charge-transfer band maximum for 1-methyl-4-carbomethoxy-pyridinium iodide correlate, in a given solvent pair, with the  $Y$  values, thus introducing a new measure of solvent "ionizing power" which may prove useful [Kosower (131)]. The rates of solvolysis of benzyl chloride in a number of solvents have been measured by Wilputte-Steinert & Fierens (132) who discuss the lack of correlation with the  $Y$  values; the rates of solvolysis of *p*-chloromethylanisole and *p*-chloromethyltoluene do, however, correlate nicely with the solvent  $Y$  values [Fierens (133)].

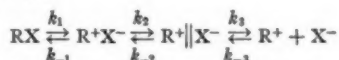
Specific solvent participation in nucleophilic displacement reactions is

discussed by Hudson (134), who finds that the rate of reaction of ethanol with certain acid chlorides in  $\text{CCl}_4$  is proportional to  $(\text{EtOH})^2$  at low  $(\text{EtOH})$  and parallels the infrared spectrophotometrically determined concentration of trimers of EtOH in the more concentrated solutions; in the donor solvent ether, where EtOH is predominantly monomeric, the order with respect to EtOH is second (135). The rate of the reaction of  $(\text{C}_6\text{H}_5)_3\text{CCl}$  with EtOH in  $\text{CCl}_4$  is proportional to  $(\text{EtOH})^2$  at low EtOH [Hudson (136)], and for the reaction of *p*-nitrobenzoyl chloride with EtOH in  $\text{C}_6\text{H}_5\text{NO}_2$ , the rate is proportional to  $(\text{EtOH})^2$  [Gilkerson (137)]. The rate of reaction of *t*-butyl chloride with acetic acid, chloroacetic acid or formic acid in nitromethane is proportional to  $(\text{RCOOH})^2$  [Boozer (138)]. The rate of hydrolysis of various acid anhydrides in acetone-water solutions has been correlated with the water content of the solvent by Koskikallio (139).

Although nucleophilic character and basicity are related, the correspondence is not exact, and thus work on the experimental establishment of nucleophilic strengths by kinetic studies and the correlation of such values with other properties continue. Bevan & Hirst (140) have established an order of nucleophilic strengths for the kinetics of displacement of  $\text{F}^-$  from *p*-fluoronitrobenzene, and de la Mare & Vernon (141) find the second order rate constant for the reaction of *t*-butyl chloride and thiophenoxide ion to be tenfold higher than the rate constants for the corresponding reactions of the stronger bases,  $\text{EtO}^-$  and  $\text{C}_6\text{H}_5\text{O}^-$ . These authors suggest that the greater polarizability of sulfide is in part responsible, and Edwards (142) has set up a nucleophilic scale which takes polarizability specifically into account.

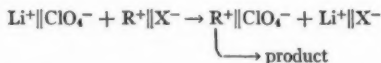
The displacement of  $\text{Br}^-$  from propyl bromide by  $\text{S}_2\text{O}_8^{2-}$  in 44 per cent ethanol has been studied by Monk (143), who shows that the transition state does not contain a metal ion ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$  or  $\text{Sr}^{++}$ ), even though thiosulfate "ion-pairs" with metal ions are believed, on the basis of conductivity data, to exist in the reaction medium. The ionic strength dependence of the rate constant for the reaction of  $\text{S}_2\text{O}_8^{2-}$  with  $\text{BrCH}_2\text{CO}_2^-$  has been the subject of another investigation (144). The kinetics of halide displacement from an alkyl halide by another halide ion (of the same or different type) have been the subject of studies by Daudel (145), Martin (146), Hughes (147) and le Roux (148).

The solvolysis reactions of alkyl halides and benzene sulfonates which do not proceed by the direct bimolecular displacement of the halide or sulfonate ion by solvent may occur via a pathway involving several different intermediates [Streitwieser (125)]. According to the kinetic scheme presented by Winstein in 1954 (149),



(where the  $\text{R}^+$  species are, from left to right, the intimate ion pair, the solvent separated ion pair and the dissociated ion), the product-forming reaction may involve any one of the "carbonium ion" intermediates. A detailed

description of some of the work of Winstein and associates which supports this picture has appeared during this year (150). Particularly interesting is the "special salt effect" observed for some reactions; for instance, the rate of acetolysis of cholesteryl toluenesulfonate is increased 65 per cent by the presence of  $4 \times 10^{-6}$  M LiClO<sub>4</sub> while a tenfold higher (LiClO<sub>4</sub>) doubles this rate enhancement. At still higher (LiClO<sub>4</sub>), the normal salt effect, a mild linear increase in rate with increasing (LiClO<sub>4</sub>), is observed. The "special salt effect" is interpreted as the intervention of Li<sup>+</sup>||ClO<sub>4</sub><sup>-</sup> at the R<sup>+</sup>||X<sup>-</sup> stage:



Thus, the limiting enhanced rate (obtained by extrapolating the linear "normal salt effect" to (LiClO<sub>4</sub>) = 0) is equal to  $\{k_1k_2/(k_{-1}+k_2)\}$  (RX). Settling the question of the relative magnitude of  $k_{-1}$  and  $k_2$  is possible for some systems; it may involve the comparison of this limiting enhanced rate with the rate of racemization of an appropriate optically active RX, which is equal to  $k_1$  (RX) (151).

Watanabe & Fuoss (152) have studied the rates of formation of the quaternary ammonium salts from *n*-C<sub>4</sub>H<sub>9</sub>Br and pyridine or 4-picoline in various solvents and find evidence for specific solvation effects superimposed on the predictable effects due to changes in dielectric constant. An incidental point of interest in this study is the decrease in rate which accompanies the precipitation of product salt in diphenyl ether solvent; this effect, opposite that expected from any heterogeneous catalysis, may be due to the reduction of the salt concentration with the occurrence of precipitation from the supersaturated solution and with it a diminution of any "salt effects" which operate in this solvent. Kauranen & Tommila do not, however, find any discontinuity in the rate with the precipitation of salt in their study of the (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N—C<sub>2</sub>H<sub>5</sub>I reaction in acetone-tetrahydrofuran solutions (153). One factor which complicates studies of this type of reaction involving polar solutes in nonpolar solvents is the nonideality of the multicomponent solutions which the reaction mixtures necessarily are; Fahim & Moelwyn-Hughes consider this carefully in their study of the reaction of CH<sub>3</sub>I and (CH<sub>3</sub>)<sub>3</sub>N in CCl<sub>4</sub> (154).

Humphreys & Hammett (155), using a stirred flow reactor, have measured the relatively high rates of alkaline hydrolysis of methyl formate (in water) and ethyl formate (in 85 per cent ethanol) as a function of temperature and find that the more positive values of  $\Delta S^\ddagger$  for the hydrolysis of the formates compared to the acetates account for the several hundredfold greater rate. Additional studies of the temperature coefficients of the rate of alkaline hydrolysis of aliphatic esters have been conducted by Fitzgerald (156), Halonen (157), Newman (158), Smith (159), Tommila (160) and Watson (161). The rates of hydrolysis and ammonolysis of methyl acetate have been determined in media containing certain  $\alpha$ -hydroxy amides [Miller &



Day (162)]. Both first and second order paths are observed in the alkaline hydrolysis of certain alkyl sulfate ions [Burwell (163)].

Tommila (164) finds the rates of the acid-catalyzed hydrolysis of certain aryl acetates in acetone-water mixtures are approximately proportional to the concentration of water. He has also reviewed solvent effects upon  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for solvolytic reactions (165). The rate of hydrolysis of chloromethyl acetate via both the HCl-catalyzed and the uncatalyzed paths have been studied by Euranto (166).

Farrington (167) has determined the rate of hydrolysis of ethyl acetate and ethyl lactate by generating  $\text{OH}^-$  electrolytically at the rate at which it is consumed in the reaction; the rate of hydrolysis of certain alkyl benzoates in concentrated  $\text{H}_2\text{SO}_4$  has been determined by measurement of the freezing point as a function of time; hydrolysis converts one solute particle into two [Leisten (168)]. Laidler (169) has measured the rate of the acid- and base-catalyzed hydrolysis of certain amides in mixed solvent and has correlated the dependence of these rates, as well as certain ester and anilide hydrolysis rates, upon the dielectric constant by means of a refined electrostatic theory. The calculated values of the radii of the activated complex seem to be reasonable.

*Studies involving the use of isotopes.*—Bell (170) has studied the deuterium isotope effect in the base-catalyzed bromination of 2-carbethoxycyclopentanone and finds an activation energy difference ( $E_D - E_H$ ) in excess of the maximum expected from the difference of zero point energies of C—D and C—H bonds; this is considered to be a demonstration of the tunnel effect operating for the hydrogen compound. It is interesting that the tunnel effect leads to an abnormally low value of  $A_H/A_D$ , the ratio of the pre-exponential factors, since "... the activation energy used in calculating  $A_H$  from the experimental results is not the actual height of the barrier,  $E$ , but an average for the systems which react, which will be smaller than  $E$ . When this is taken into account it is found the effect of tunneling is to reduce  $A$ ."

An unusually large deuterium isotope effect is observed in the cleavage of phenyl-*t*-butylcarbinol by  $\text{Cr}^{\text{VI}}$ . While the rate factor  $k_H/k_D = 10$  is not too large to be explained by the usual means, Westheimer speculates that the reason may be a contribution to the reaction by a branching chain path involving C—H bond breaking, thus magnifying the normal isotope effect (171). Of two  $\text{Cr}^{\text{VI}}$  oxidation reactions shown to involve C—H bond breaking in the rate-determining step, Ropp & Hodnett (172) find a  $\text{C}^{14}$  isotope rate effect in one of the reactions. The isotope rate effect in the  $\text{OH}^-$  catalyzed exchange of  $\text{CDCl}_2\text{F}$  and water suggests that hydrogen is rather tightly held in the transition state [Hine (173)]. The influence of the substitution of deuterium at the alpha-carbon or at the beta-carbon in phenyl cyclopentyl and phenyl cyclohexyl ketones upon the acid- and the base-catalyzed enolization rates has been investigated by Emmons & Hawthorne (174). Melander (175) tentatively suggests that a correlation exists between the reactivity of an aromatic ring position and the value of  $k_T/k_D$ , the ratio of

the rates of exchange of T and D between the appropriately tagged hydrocarbon and concentrated  $\text{H}_2\text{SO}_4$  (80.8 per cent in the experiments reported). An isotope effect  $k_{\text{H}}/k_{\text{D}} = 1.84$  is observed for hydride ion transfer in the reaction of isopropanol and  $(\text{C}_6\text{H}_5)_3\text{C}^+$  in concentrated  $\text{H}_2\text{SO}_4$  [Bartlett (176)]. An example of a deuterium substituted compound reacting more rapidly is provided by the work of Lewis (177) on the decomposition of *p*-toluenediazonium ion. Since the effect is small ( $k_{\text{H}}/k_{\text{D}} = 0.99$ ), methods were developed for performing the experiments and treating the data which have eliminated many analytical errors.

Yankwich (178) has continued his carbon isotope effect work with a study of the intramolecular carbon isotope effect in the decarboxylation of hydrogen malonate ion in quinoline solution; Grigg (179) has studied malonic acid at its melting point and also in quinoline.

Since  $\text{D}_2\text{O}$  is a less basic solvent than  $\text{H}_2\text{O}$ , protonated solute species are more stable relative to the corresponding conjugate bases in  $\text{D}_2\text{O}$ . This leads to an approximately twofold greater rate in  $\text{D}_2\text{O}$  for reactions in which an equilibrium to give a protonated species precedes the reaction of this species in the rate-determining step. This is observed in the acid-catalyzed hydrolysis of certain epoxides studied by Pritchard & Long (180). In the hydration of olefins, however, Purlée & Taft (181) observe  $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} \cong 1$  because the factor of 2, mentioned above, is offset by isotope rate factor,  $k_{\text{D}}/k_{\text{H}} \cong 0.5$ ; here the rate-determining step involves the added proton, which was not the case in the epoxide hydrolysis. That in both of these reactions the acid catalysis is due to the formation of the protonated species prior to the rate-determining step follows from the conformity of the rate data in  $\text{D}_2\text{O}$ — $\text{H}_2\text{O}$  mixtures to the Butler equation. The pinacol-pinacolone rearrangement, which is subject to specific hydrogen ion catalysis in dilute acidic solutions (182) and in more concentrated  $\text{HClO}_4$  solutions shows a correlation between the rate and  $H_0$ , proceeds 2.2-fold more rapidly in  $\text{D}_2\text{O}$  than in  $\text{H}_2\text{O}$  solution (183); it has also been shown by the use of  $\text{O}^{18}$  that 60 per cent of the carbonium ions formed return to pinacol (184). Laughton & Robertson (185) have studied the solvolysis of certain benzene sulfonic esters in  $\text{D}_2\text{O}$  and conclude that an important factor influencing the value of  $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}$  is the nature of the anion being formed in the reaction.

The very rapid exchange of hydrogen between *t*-butanol and triphenylcarbinol in toluene solution has been studied by Swain & Halman using a flow apparatus; the reaction is zero order in *t*-butanol (186).

The exchange of oxygen between water and the carboxylate group of an ester or acid may proceed via an addition intermediate  $\text{RC}(\text{OH}_2)\text{OR}'$  (where  $\text{R}'$  may be H), and thus observed exchange is viewed as evidence for the existence of such a species. Bender (187) observes that methyl 2,4,6-trimethylbenzoate undergoes such exchange during its alkaline hydrolysis in 60 per cent dioxane with  $k_{\text{hyd}}/k_{\text{exch}} = 6.8 \pm 0.5$ ; no exchange is observed by Bunton (188) in the alkaline hydrolysis of phenyl benzoate in 50 per cent dioxane. Bender (189) observes oxygen exchange between certain substituted

benzoic acids and water under acidic conditions (0.07 *N* HCl in 33 per cent dioxane), the rate paralleling the rate of acid hydrolysis of the corresponding ethyl ester.

*Metal ion or metal compound-promoted reactions.*—Transition states involving metal ions are important in a number of hydrolysis and decarboxylation reactions; structurally these transition states may resemble the complex ions which exist in some of the systems although the kinetic demonstration of a transition state  $MX^a$  does not, in itself, demand any structural similarity to the complex ion  $MX^a$ . The rare earth ions catalyze the decarboxylation of oxaloacetic acid with an effectiveness which parallels the stability of the  $M(C_4H_5O_6)^+$  complex except in the case of the paramagnetic ions  $Gd^{+++}$  and  $Dy^{+++}$  which are, respectively, 25 per cent and 15 per cent more effective [Gelles (190)]. Copper(II) ion is a very effective catalyst for the hydrolysis of glycine amide and phenylalanine-glycine amide [Westheimer (191)] and for the decarboxylation of hydroxytartaric acid [Pedersen (192)]. Beringer (193) has observed a dramatic copper(I) chloride catalysis of the formation of  $C_6H_5Cl$  and  $C_6H_5I$  from  $(C_6H_5)_2ICl$  in ethylene glycol.

Metal compounds which are good Lewis acids are effective catalysts for certain reactions in aprotic solvents; kinetic studies on the  $AlBr_3$ -catalyzed isomerization of ethyl-[1- $C^{14}$ ] bromide and the related bromine exchange between  $C_2H_5Br$  and  $AlBr_3$  have been reported [Sixma (194)]. In their kinetic study of the exchange between  $SnCl_4$  and 2-chlorobutane in heptane, Howald & Willard (195) demonstrate the existence of a 1:1 complex of these molecules.

*Nonpolymerization radical reactions.*—From a comparison of the rate of racemization of 2-iodobutane and its rate of iodine exchange with  $I_2$  in  $C_4Cl_8$  solvent, Noyes (196) concludes that the radical inversion reaction  $d BuI + I_2 \rightleftharpoons BuI + I$  does occur although an alternate interpretation is also presented. Another reaction involving iodine atoms is the chain reaction of 4-camphylmercuric iodide and iodine, the rate of which is proportional to  $(I_2)^2$  [Winstein (197)].

Metal ion catalysis via the chain initiating step in certain autoxidation reactions has been studied by Bawn (198) and Uri (199). The rate of oxidation of isobutyraldehyde by the radical  $ON(SO_3)_2^{\cdot -}$  is proportional to  $(ON(SO_3)_2^{\cdot -})(RCHO)(OH^-)$  and is lower than the rate of the corresponding oxidation by  $Fe(CN)_6^{\cdot -}$  which is zero order with respect to  $Fe(CN)_6^{\cdot -}$ ; thus a lower reactivity of  $ON(SO_3)_2^{\cdot -}$  than  $Fe(CN)_6^{\cdot -}$  toward enolate ion is indicated [Waters (200)]. The kinetics of the reaction of cumene hydroperoxide and iron(II), as the aquo ion, versenate complex or pyrophosphate complex, have been studied by Reynolds & Kolthoff (201). The rates of decomposition of dibenzoyl peroxide and di- $\alpha$ -cumyl peroxide in cumene have been studied by Bailey & Godin (202) who find the reaction of the latter compound is not a chain reaction. Such is also the case for the reaction of phenol with benzoyl peroxide in solvents which do not readily donate a hydrogen atom to radicals [Batten (203)].

Szwarc has continued his work in this area with studies of the ethyl affinities of a number of aromatic substances, the correlation of methyl affinities of certain aromatic compounds with the corresponding localization energies, and the reactions of methyl radicals with olefinic or aromatic compounds which can act as methyl radical acceptors or hydrogen atom donors (204). Hydrogen abstraction by *t*-butoxy radicals leads to *t*-butanol, and radical decomposition leads to acetone; Williams *et al.* (205) have studied the yields of these products with a large number of hydrocarbons in order to determine the relative reactivity of different "types" of hydrogen atoms.

Szwarc has studied the decomposition of propionyl and butyl peroxides in a variety of solvents; the appropriate use of a scavenger demonstrates a "cage" combination of ethyl radicals from  $(C_2H_5COO)_2$  to form  $C_4H_{10}$  (206).

*Reactions in aromatic systems.*—The work of Ainscough & Caldin on the kinetics of the reactions of  $OEt^-$  and aromatic nitro compounds is particularly interesting (207). Trinitroanisole forms two different 1:1 compounds with  $OEt^-$ ; the rate of formation of the one, assumed to be a charge transfer complex, is measurable in the range  $-80^\circ$  to  $-60^\circ C.$  and the other in the range  $-20^\circ$  to  $+10^\circ C.$  Both the rate of formation of these "compounds" and the rates of decomposition with acids have been measured. The rate constants for the reaction of the more labile of these "compounds" with different carboxylic acids are consistent with the Brönsted equation.

The iodination of *p*-chloroaniline with  $ICl$  in aqueous media proceeds via a transition<sup>†</sup> state of the composition  $ClC_6H_4NH_2 \cdot I(OH_2)_n^+$  [Berliner (208)]. In addition to determining the rate of bromination of toluene with  $HOBr$ , De la Mare (209) has determined the relative amounts of the isomeric products which are formed. The partial rate factors in other aromatic reactions have been reported [Dewar (210); Gold (211); Tiers (212)]. Keefer & Andrews have studied the uncatalyzed and  $ZnCl_2$ -catalyzed halogenation of certain polymethylbenzenes in acetic acid solution (213). The bromodecarboxylation of certain dibromohydroxybenzoic acids has been studied kinetically by Grovenstein (214). A review pertaining to the kinetics and mechanism of electrophilic aromatic substitution has appeared by Zollinger (215).

The  $AlBr_3$ -catalyzed reaction of benzene and toluene with  $RBr$  in 1,2,4-trichlorobenzene is first order in  $AlBr_3$  [Brown (216)] while the corresponding  $GaBr_3$ -catalyzed alkylation in benzene or toluene as solvent is second order in  $GaBr_3$  [Brown (217)]. Kinetic studies of the exchange of hydrogen between  $HCl$  and toluene catalyzed by  $SnCl_4$  or  $NO_2$  have been made by Willard (218).

*Organophosphorus compounds.*—The hydrolysis of Sarin, isopropyl methylphosphonofluoridate, is catalyzed by certain reagents, the identity of which makes it clear that basicity and nucleophilicity are not the only factors contributing to the catalytic efficiency. The kinetics of the reaction

of Sarin with  $\text{OCI}^-$  and certain substituted catechols have been studied by Epstein *et al.* (219); if one considers only the catechols, the rate constants and the basicity are related by the Brönsted relationship with an exponent of 0.89. Kinetic studies on the reaction of Sarin with benzohydroxamic acid (220) and certain oximes (221) have also been reported. In the case of the reaction of paraoxon,  $(\text{C}_2\text{H}_5\text{O})_2\text{PO}(\text{OC}_6\text{H}_4\text{NO}_2)$ , with peroxide, the second order reaction which involves the peroxide anion accomplishes, as a net result, both the hydrolysis to yield nitrophenol and the decomposition of peroxide [Epstein (222)]. The rate of hydrolysis of the sulfur analogue parathion,  $(\text{C}_2\text{H}_5\text{O})_2\text{PS}(\text{OC}_6\text{H}_4\text{NO}_2)$ , is increased twentyfold by  $3 \times 10^{-7} M \text{ Cu}^{++}$  [Ketelaar (223)].

The rate of hydrolysis of cyclic ethylene phosphate ion has been found to be  $>10^6$ -fold larger than the hydrolysis rate of dimethyl phosphate; Westheimer also shows that a transition state involving  $\text{Ba}^{++}$  provides an important reaction pathway (224). Since  $((\text{CH}_3)_2\text{N})_2\text{PO}(\text{Cl})$  hydrolyzes at a rate which is independent of the concentration of base, Hall (225) concludes an  $\text{S}_{\text{N}}1$  mechanism is operating. Additional kinetic studies on the hydrolysis of organophosphorus compounds have been carried out by Hudson (226) and Heath (227).

*Miscellaneous organic reactions.*—De Tar has studied the rate of decomposition of certain benzene and naphthalene diazonium ions (228); while these reactions in aqueous acidic solution proceed in an uncomplicated first order manner, the decomposition of benzenediazonium ion in acetate-buffered methanol proceeds via a radical chain mechanism which is influenced by oxygen. Kinetic studies have also been made on the first order decomposition of *o*-nitrophenyl azide in several solvents and in the pure liquid (229), phenylazotriphenylmethane in several solvents (230), thiourea in aqueous solution (231) and nitramide in dioxane-water mixtures (232).

The two step alkaline hydrolysis of acetonitrile has been studied by Widequist (233), who points out that the expression for  $d(\text{NH}_3)/dt$  is symmetrical in the rate constants for the two steps; thus a particular kinetic behavior does not uniquely establish both  $k_1$  and  $k_2$ . The rates of both the forward and reverse reactions have been studied in the hydrolysis of benzalaniline (234) and in the stepwise esterification of butanediol with acetic acid (235).

The base-catalyzed condensation of 3-methyl-6-benzalcylohexanone with benzaldehyde is the subject of a kinetic study by Kresze & Gnauck (236), and a kinetic study of the Cannizzaro reaction of glyoxal has been made by Salomaa (237). The temperature coefficients of the rate of formation of several oximes have been established by the work of Gettler (238).

The dimerization of acetyl cyanide which proceeds via the cyanohydrin follows a reasonably simple kinetic pattern if excess HCN and pyridine are present; Tate & Bartlett (239) have studied this reaction in acetonitrile solution. Schmid (240) has continued his studies of the rate of diazotization,

and Leffler (241) continues his studies on the variation of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  with solvent and structure. The reaction of barbituric acid and  $\beta$ -nitrostyrene has been studied by Kamlet & Glover (242).

#### ENZYME-CATALYZED REACTIONS

Enzyme-catalyzed reactions provide examples of kinetic complexity which tax the application of simple physical chemical principles. Although this area has not been reviewed in the past few years, the limitation of space confines this discussion to publications of the past year which include papers and the associated discussion from the Faraday Society meeting of August, 1955 dealing with the physical chemistry of enzymes (including kinetic behavior) (243) and review papers by Alberty (244, 245).

Transient state kinetic data furnish more information regarding reaction mechanism than steady state data and thus the mathematical contributions of Gutfreund (246), Ouellet & Laidler (247) and Greenstein (248) are of interest. The outstanding application of transient state kinetic data has been that by Chance [reviewed in (244)]. The fact that inhibition of catalase activity by certain anions, with which the enzyme has been pre-equilibrated, increases progressively after the introduction of the substrate indicates an interaction of the inhibitor with ES and not exclusively with E [Beers & Sizer (249)]. Because of the lack of sufficiently rapid and sensitive analytical methods or more fundamental limitations imposed by the chemical system itself, many enzyme kinetic studies have been (and will be) carried out under steady-state conditions. For this reason the derivation of the steady state rate equations corresponding to various mechanisms is of fundamental importance. Ogston (250) discusses certain aspects of the subject. Laidler (251) has derived the rate equations for a two substrate system involving the intermediates ES, ET, and EST, and King (252) presents a rapid method for deriving such rate equations. Mechanisms of this type, which involve more than one pathway for enzyme catalysis, can give rise to an unusual kind of kinetic behavior which cannot arise in single pathway mechanisms [King (253)]. The evaluation of rate constants is discussed by Slater (254), and Niemann (255) has developed a method for the evaluation of the steady state velocity corresponding to  $(S) = (S)_0$  which does not depend upon any assumptions regarding the form of the rate law.

Laidler (256) discusses the influence of temperature, pressure and dielectric constant on the rate of enzymatic reactions. Experimentally observed dependence of the activation energy upon temperature is the subject of a paper by Hultin (257).

In many systems the influence of pH upon reaction velocity is marked; the bell shaped plots of the maximum initial velocity versus pH have been interpreted in terms of the participation of two ionizable groups of the ES complex as originally suggested by Michaelis in 1911. Certainly the detailed studies of fumarase by Alberty (245) are amenable to such an interpretation.

Bergmann's study of the activity of several esterases reveals optimum pH values (258); in the case of chymotrypsin catalysis, different results have been reported by Gutfreund (259), who observes a plateau in  $k_3[E]$  versus pH at pH > 8.2 for the hydrolysis of acetyl-L-phenylalanine ethyl ester (pH = 9 is maximum pH studied), and by Laidler (260), who observes a decrease in  $k_3[E]$  with an increase of pH in the pH range 7.8–8.4 for the hydrolysis of methyl hydrocinnamate; these data suggest the pK values for ES depend upon the nature of S. The activity of ficin shows a plateau in activity at high pH (261).

A different interpretation of the bell-shaped curves is Kirkwood's fluctuation mechanism for which but a single kind of ionizable group is required; the maximum activity occurs at pH = pK, the pH value at which half of the groups are ionized, and the charge fluctuations are, therefore, maximal (262).

A bell shaped plot of  $V_{\max}$  versus  $(\text{Co}^{++})$  for glycylglycine dipeptidase activity indicates that at high values of  $(\text{Co}^{++})$  the transition-state involves fewer atoms of  $\text{Co}^{++}$  than are associated with the enzyme [Rabin (263)]. Kinetic studies have demonstrated the inhibition of yeast invertase by  $\text{UO}_2^{++}$ ,  $\text{Ag}^+$ ,  $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$  and  $\text{Zn}^{++}$  [Myrback (264)]. In contrast to such metal ion inhibition, studies by Raaflaub (265) demonstrate the catalytic effects of  $\text{Ca}^{++}$  on phosphatase and  $\text{Mg}^{++}$  on hexokinase, which operate only in an intermediate pH region ( $\sim 4$  to 6). Hoch & Vallee (266) have investigated the role of  $\text{Zn}^{++}$  in the activity of yeast alcohol dehydrogenase.

Fergusson (267) finds the rate of formation of peroxidase complex-I with  $\text{IrBr}_6^-$  as the oxidizing agent is independent of the concentration of  $\text{IrBr}_6^-$ , thus reopening the question of the nature of the intermediates in the peroxidase-peroxide reaction. Studies which demonstrate the existence and kinetic behavior of monoacetylchymotrypsin, an intermediate in the chymotrypsin-catalyzed hydrolysis of *p*-nitrophenyl acetate, have been published by Neurath (268) and Gutfreund & Sturtevant (269). Vaslow (270) has studied the oxygen exchange between water and N-acetyl-3:5-dibromo-L-tyrosine catalyzed by chymotrypsin. The dependence of the catalytic activity of this enzyme upon the concentration of NaCl and KCl has been studied by Niemann (271). The complicated effects of various salts on the activity of urease have been investigated by Kistiakowsky (272).

From the temperature dependence of the catalytic activity of acetyl cholinesterase toward several substrates, Wilson (273) has calculated values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ . The nature of this enzyme has been probed by various inhibition studies [Friess (274); Bergmann (275)]. The use of certain phosphate esters as insecticides and chemical warfare agents is based upon their inhibition of this enzyme; several studies on such inhibition and its reversal have appeared (276, 277, 278). Studies on ester hydrolysis catalyzed by horse liver esterase have been interpreted in rather different mechanisms by Kistiakowsky (279) and Christiansen (280).



Kinetic studies of the reversible reaction of aldehyde and reduced diphosphopyridine nucleotide, DPNH, to yield alcohol and oxidized diphosphopyridine nucleotide, DPN, catalyzed by alcohol dehydrogenase, ADH, by Theorell and co-workers have continued (281). A three-step mechanism involving the binary complexes  $DPNH \cdot ADH$  and  $DPN \cdot ADH$  (but no ternary complex) is consistent with the data; all six rate constants were evaluated from steady state studies on the forward and reverse reactions. A similar mechanism is followed if DPN and DPNH are bound to glyceraldehyde-3-phosphate dehydrogenase [Nygaard (282)]. Kinetic studies on the reaction of this same oxidation-reduction couple, DPN-DPNH, with the lactate-pyruvate couple catalyzed by lactic dehydrogenase have been made by Nygaard (283) and Schwert (284).

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## ORGANIC REACTION MECHANISMS<sup>1,2</sup>

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Much research was done on elucidation of organic reaction mechanisms in 1956. This review attempts to cover only those reactions which, in the opinion of the reviewers, are of general importance or illustrate sufficiently novel techniques to be of widespread interest. We have not deemed it necessary to restrict attention to those reactions for which kinetic data are available to establish the molecularity of the transition state. Instead "reaction mechanism" has been interpreted in its broadest sense, namely the manner in which the reactants are converted into products. As a result, considerable attention has been focused on product-determining processes involving unstable intermediates even when the kinetics and mechanism(s) by which the intermediates themselves are formed may be unknown or imperfectly known. No effort has been made to include pure reactivity studies, however interesting for other reasons, which do not give direct new information about reaction mechanisms. A number of important studies have been omitted from this review which are adequately covered in the chapter by King (see page 273).

*Books.*—Among the books published dealing with organic reaction mechanisms and related topics in 1956, special mention seems deserved by Hine's general text, *Physical Organic Chemistry* (1), Leffler's *The Reactive Intermediates of Organic Chemistry* (2), and Newman's *Steric Effects in Organic Chemistry* (3).

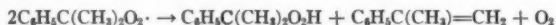
### OXIDATION AND REDUCTION

*Oxidation by oxygen.*—The year saw a continuation of the lively interest in low-temperature, liquid-phase oxidations. A solution to the classic problem of formulating the mechanism of uninhibited chain termination has been provided by Boozer *et al.* (4) and by Russell (5). The former group measured the effect of deuteration of the methyl groups of cumene on the

<sup>1</sup> The survey of literature pertaining to this article includes the available journals of November, 1956.

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over-all rate of initiated oxidation and separated the effects on chain propagation and chain termination by the use of inhibitors. The residual effect on the termination reaction points to the involvement of  $\beta$ -hydrogens, indicating that a disproportionation mechanism or its equivalent must occur.

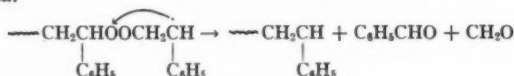


Russell showed that  $\alpha$ -hydrogens are involved in the termination reactions of  $\alpha$ -phenylethylperoxy radicals by the same technique. A slight looseness in the argument involves the assumption that the isotope effect on the chain-carrying hydrogen abstraction reaction is the same for  $\alpha$ -deuteriocumene and  $\alpha$ -deuteroethylbenzene. However, the  $k_{\text{H}}/k_{\text{D}}$  ratio (1.9) estimated for the termination reaction is substantial and the isotope effect on propagation might be expected to be larger in the ethylbenzene propagation rate than in the comparable reaction of cumene. Infrared analysis of oxidation mixtures shows the presence of carbonyl groups in amounts predicted by the following termination reaction.

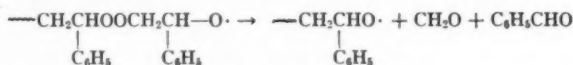


The results of the two studies serve to explain the superiority of secondary peroxy radicals over tertiary in chain termination [Russell (6, 7)].

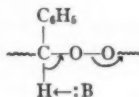
Miller & Mayo (8) reported a thorough investigation of the reaction of styrene with oxygen. A chain process is initiated either thermally or by azobisisobutyronitrile. Thermal initiation involves oxygen and styrene. The reaction produces formaldehyde, benzaldehyde, and polymeric peroxide. The yield of aldehydes is controlled by the oxygen pressure under conditions where the over-all rate is oxygen independent. An interesting, "unzipping" reaction of styrene-terminated, polyperoxide radicals is invoked to account for the data.



The photochemical and thermal degradation of styrene peroxide [Mayo & Miller (9)] also produces substantial amounts of aldehydes, probably by the depolymerization of alkoxy-terminated radicals.



Base-catalyzed degradation of the polymer produces hydroxyketone units, lending generality to a mechanism discovered some years ago by Kornblum & De La Mare (10).



Russell (11) has shown that the initiated reaction of indene with oxygen produces a copolymer, indicating that the addition of peroxy radicals to indene is preferred to the competing hydrogen abstraction from the activated methylene group. Reduction of the polymer with lithium aluminum hydride gives a mixture of *cis*- and *trans*-indene glycols showing that the addition reaction is nonstereospecific. A careful comparison of the thermal- and azo-initiated reactions shows that the same intermediates are involved in the two processes, contrary to an earlier suggestion by Mulcahy & Watt (12). As in the case with the styrene-oxygen system, careful attention was accorded the nature of the thermal initiation step and it appears that nonphotochemical, initiating reactions between oxygen and hydrocarbons have been rigorously established for the first time.

Bickel & Kooyman (13) reported a classic study of the rates of oxidation of 9,10-dihydroanthracene in the presence of phenolic retarders. Three different rate laws were observed. The authors suggest that the variation may be attributed to combinations of reversible and irreversible interactions of growing chains with retarder molecules. Their particular suggestion embodies hydrogen abstraction from the phenol as the key step in the over-all process. Present information does not seem to give an unambiguous choice between rapid hydrogen atom transfers and other possible reversible interactions between chain carriers and inhibitors.

Bawn *et al.* (14, 15) investigated the kinetics of metal-ion catalyzed oxidations of benzaldehyde and acetaldehyde in acetic acid solution. The initiation step is believed to be a one-electron oxidation of the aldehyde to an acyl radical.

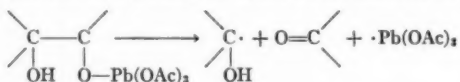


The metal ion is subsequently reoxidized by peracid, the first oxidation product. The kinetics fit the proposed initiation mechanism during a steady period which follows an initial slow stage. The induction period is considered to be required for establishment of the steady state level of oxidized and reduced forms of the metal ion. It is asserted that the oxidation of peracid by the higher valence state of the metal does not contribute to chain initiation since a mechanism involving the reaction cannot be fitted to the simple rate law,  $v = k[\text{RCHO}]^{3/2}[\text{Metal}]^{1/2}$ .

*One-electron oxidants.*—Reference is made to a number of such reactions in connection with redox initiator systems and the arylation of alkenes by the Meerwein reaction. Haynes, Turner & Waters (16) have made a preliminary survey of the reactions of phenols with potassium ferricyanide. Although the reactions are disagreeably complicated, the data indicate that the initial step is a reversible electron transfer from phenoxide to ferricyanide. Allen & Waters (17) have shown that the ion radical, nitrosyldisulfonate, oxidizes aldehydes in a base-catalyzed reaction. The mechanism is formulated as a rate-determining electron transfer from the enolate ion to nitrosyldisulfonate anion. The kinetic data show less than an ideal correlation

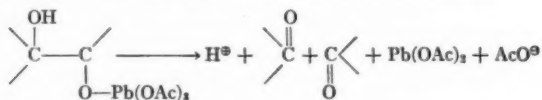
with the mechanism since the order with respect to hydroxide is below unity in buffered solutions and the salt effect is negative.

Levesley, Waters & Wright (18) advocate that the oxidation of glycols by lead tetraacetate, long considered to be a two-electron change with a cyclic ester as a key intermediate, be reconsidered. The much revered stereospecificity of the reaction appears to be largely mythical since the large difference in rate between *cis*- and *trans*-cyclohexanediols is not sustained with the 1,2-dimethyl-1,2-cyclohexanediols and *trans*-1,2-dimethyl-1,2-cyclopentanediol. There are some similarities between the series of reactivities observed in lead tetraacetate oxidation and that describing reactivities toward manganic pyrophosphate, a legitimate one-electron oxidant. In particular, *trans*-dimethylcyclopentanediol is relatively reactive toward both reagents. If the rate-determining step of lead tetraacetate oxidation is a one-electron transfer it could be formulated as follows:



The excellent stoichiometric relationships would then require that the hydroxyalkyl radicals must infallibly react with either lead tetraacetate, lead triacetate or acetoxy radicals (from the fragmentation of lead triacetate). The authors fail to comment explicitly on the possible occurrence of two-electron transfers not involving cyclic esters but clearly have not rejected such possibilities.

A somewhat different point of view is taken by Criegee *et al.* (19) of glycol cleavage by lead tetraacetate. These workers found the rates of a large number of 1,2-glycols to vary by factors up to  $10^7$ , and to be insensitive to radical chain inhibitors. The rates roughly increase as the hydroxyls can come close together, but exceptions are found. Both cyclic and noncyclic mechanisms of the following type were postulated to operate.



*Chromic acid oxidations.*—Hampton, Leo & Westheimer (20) have made an elegant study of the simultaneous oxidation and cleavage of phenyl-*t*-butylcarbinol with chromic acid in 86.5 per cent acetic acid. The ratio of normal oxidation product, phenyl *t*-butyl ketone, to cleavage products, benzaldehyde and *t*-butyl alcohol was found to be a sensitive function of the reaction conditions. Maximum cleavage ( $\sim 67$  per cent) was observed in acetate-buffered dilute chromic acid solutions. Cleavage was suppressed in the presence of concentrated chromic acid or dilute solutions of manganous or cerous salts. The  $\alpha$ -deuterated<sup>1</sup> carbinol is both oxidized and cleaved about 1/10 as fast as the ordinary carbinol. The extent of cleavage is gen-

erally higher with the deuterated alcohol. These facts are in agreement with the earlier views [Westheimer (21)] that the normal oxidation involves a rate-determining attack of water (or other base) on the  $\alpha$ -hydrogen of the alcohol chromate ester yielding ketone and Cr(IV). Cleavage is inferred to be the result of attack of Cr(V) [from reaction of Cr(IV) with Cr(VI)] on the alcohol. The H-D isotope effect in the oxidation of the deuterated alcohol was observed to be a factor of 12 at 0°. This rather abnormally high isotope effect could be due to "tunnelling," unusually low frequency C-H bending vibrations in the transition state, or possibly to a branching-chain oxidation sequence which might be particularly sensitive to a normal kinetic isotope effect.

*Oxidations with manganese compounds.*—Wiberg & Stewart (22) have made a careful study of the oxidation of formate ion to carbonate ion by permanganate and confirmed earlier work by Tompkins (23, 24) regarding the lack of pH dependence, positive salt effect and the greater rate of reaction of formate compared to formic acid. The H-D kinetic isotope effect was shown to be 7.4 indicating a slow hydrogen transfer in the rate-determining step. About one-third of the oxygen picked up by formate in the oxidation to carbonate was found to be derived from permanganate by use of  $O^{18}$ -labeled permanganate. The fact that formate is oxidized faster than formic acid taken with the isotope effect suggests that the transition state cannot be essentially a formate-permanganate complex but must have the C-H bond well broken and an oxygen being transferred from manganese to carbon.

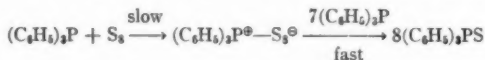
A similar investigation of the H-D isotope effect in oxidation of formate has been reported by Aebi, Buser & Lüthi (25). The reported value of  $k_H/k_D$  was 6–10.

*Hydride ion transfers.*—Bartlett & McCollum (26) have investigated hydride ion transfers in the oxidation of alcohols by di- or triarylmethyl cations in strong acid solutions. A typical reaction of this variety is the oxidation of isopropyl alcohol to acetone by triphenylcarbinol or dianisylcarbinol in 20 to 40 per cent sulfuric acid. The reduction products are the di- or triarylmethanes. These reactions were shown to involve a shift of the hydrogen of the isopropyl alcohol directly to the carbocations by the reaction kinetics and by deuterium tracer studies. The H-D kinetic isotope effect was found to be about a factor of two. The entropy of activation of these reactions indicate that the transition state is highly congested in accord with the postulated mechanisms.

*Sulfur.*—The oxidation of triarylphosphines to triarylphosphine sulfides with elemental sulfur in relatively nonpolar solvents has been thoroughly studied by Bartlett & Meguerian (27). The reaction is bimolecular, first order in each participant and the rate constants are quite solvent sensitive, changing around 100 fold between chlorobenzene and cyclohexane. The solvent effect indicates a substantial charge separation in the transition state. The rates of a number of *p*-substituted triphenylphosphines were



determined and Hammett's  $\rho$  constant found to be  $-2.5$ . The rate-determining step of the reaction was postulated to be attack of triphenylphosphine on  $S_8$  in a Menschutkin-type process with subsequent reactions of the open sulfur chain being fast. It was demonstrated that  $S_8$  reacts many times



more readily than  $S_8$  with phosphines. Sulfur dissolved in benzene irradiated with sunlight for three hours was converted to forms, 78 per cent of which reacted more than  $100\times$  faster with triphenylphosphine than nonirradiated  $S_8$  under the same conditions.

*The Sommelet reaction.*—Franzen (28) treated  $\alpha,\alpha$ -dideutero benzylamine with hexamethylenetetramine in acid solution, and obtained deuterobenzaldehyde and  $\alpha$ -deuteromethylamine. The reaction was uncatalyzed by complexing heavy metals, and is considered to proceed by hydride ion shift from amine to imine cation.

#### ELECTROPHILIC AROMATIC SUBSTITUTION

*Halogenation.*—Keefer & Andrews (29 to 32) have studied the halogenation of polymethylbenzenes in acetic acid solutions. Bromination of mesitylene (29) was found to proceed by two independent mechanisms each apparently involving reaction of a bromine-mesitylene complex with an electrophilic reagent which functions to remove bromide ion. Bromine itself is effective in this role—much more so than acetic acid which was found to be quite weak. Zinc chloride is a powerful catalyst, and its effectiveness was studied separately as a function of hydrocarbon structure (30). Substantial steric effects were noted.

*Friedel-Crafts reactions.*—Brown & Jungk (33) have studied Friedel-Crafts type alkylation of benzene and toluene with alkyl halides in a rapid-flow system. Contact times were on the order of 0.005 sec. to minimize side reactions. The alkylation was expressed mechanistically by attack of an aluminum bromide-alkyl halide complex with a polarized C-Br bond on the hydrocarbon. The complex is essentially a carbonium ion- $AlBr_4^-$  ion pair. Jungk, Smoot & Brown (34) studied the kinetics of aluminum bromide-catalyzed alkylations of benzene and toluene with methyl and ethyl bromides in 1,2,4-trichlorobenzene solutions (homogenous). The rate was first order in each participant,  $d[HBr]/dt = k[RBr][AlBr_3][RH]$ . It was concluded that the active species attacking the aromatic hydrocarbon was not the free carbonium ion but probably a halide-aluminum bromide complex.

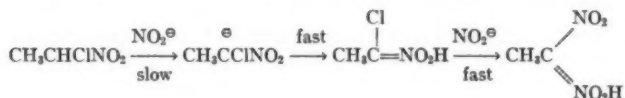
#### ALIPHATIC SUBSTITUTION

Mechanisms for substitution reactions of allylic compounds have been reviewed by de Wolfe & Young (35). The effects of conformational variables

on the course of reactions of alicyclic compounds have been discussed in detail by Barton & Cookson (36).

*Solvolytic substitution reactions.*—The current mechanistic situation for solvolytic displacement at saturated carbon atoms has been reviewed by Streitwieser (37).

*Bimolecular substitution reaction.*—Hawthorne (38) showed that the reaction of nitrite ion with  $\alpha$ -chloronitroethane (ter Meer reaction) is consummated by displacement of chloride from the chloronitronic acid. The reaction is first order with respect to nitrite, shows a primary isotope effect if the  $\alpha$ -hydrogen is replaced by deuterium and is completely inhibited by conversion of the substrate to the chloronitro carbanion with strong base.



The author suggests the other displacement reactions of halonitro alkanes may involve similar mechanisms.

*Oxide and imine-ring openings.*—Brewster (39) has demonstrated that the epoxide of *trans*- $\alpha$ -methylstilbene opens with retention of configuration upon acid hydrolysis. Curtin *et al.* (40) observed that *cis*- and *trans*-*p*-methoxystilbenes react with perbenzoic acid to give predominantly the glycol monobenzoate formed by over-all *cis*-addition of the elements of perbenzoic acid to the double bond. *trans*-*p*-Methoxystilbene oxide was found to react with benzoic acid in chloroform to give predominantly *threo*-hydroxybenzoate, the ring opening having occurred with retention of configuration. The possible similarities between these *cis*-ring-openings and the  $\text{S}_{\text{N}}1$  reaction are pointed out.

Pritchard & Long (41) have made a very careful study of the hydrolysis of ethylene oxide derivatives. In the acid-catalyzed reactions, all of the logarithms of the rate constants were accurately linear with Hammett's  $\text{H}_0$ . With propylene oxide, ring-opening was shown with  $\text{O}^{18}$ -water to occur predominantly (66 to 74 per cent) but not exclusively at the secondary carbon. Isobutylene oxide gave only ring-opening at the tertiary carbon. The variation of the acid-catalyzed reaction rate with solvent composition in  $\text{H}_2\text{O}$ — $\text{D}_2\text{O}$  mixtures strengthens the postulate of an equilibrium proton transfer ahead of the rate-determining step. It was concluded that the acid-catalyzed ring-opening of oxides involves a slow carbonium ion formation from the conjugate acid of the oxide. While such a mechanism is not only possible but, in fact, probable for isobutylene oxide, it seems much less likely for ethylene and propylene oxides. The crucial point seems to be the validity of excluding nucleophilic attack of a water molecule on the conjugate acid of the oxide because of the linear variation of  $\log k$  with  $-\text{H}_0$  (42). The results of Buntin, Konasiewicz & Llewellyn (43) demonstrate that optically-

active *s*-butyl alcohol racemizes in aqueous perchloric acid containing  $O^{18}$  by a reaction having a linear variation of  $\log k$  with  $H_0$  but with clean inversion of configuration with each oxygen exchange of the alcohol. These observations appear to vitiate some of the force of mechanistic arguments based on linear relationships between  $\log k$  and  $H_0$ .

The polymerization of trimethylene oxide derivatives induced by boron trifluoride has been studied by Rose (44). A long chain polymer and a crystalline, cyclic tetramer were the major products. The proportion of tetramer increased with temperature to a maximum of about two-thirds of the product. Hydroxyl compounds (ethanol, water, hydroxyl-terminated polymer) act as cocatalysts. The reaction rate is proportional to  $k[\text{monomer}][\text{BF}_3][\text{ROH}]$  at low ROH concentrations. The kinetics are in accord with chain-growth by attack of a cyclic oxonium salt  $\text{HO}(\text{CH}_2)_3\text{O}[(\text{CH}_2)_3\text{O}]_{n-2}\text{CH}_2-\text{CH}_2-\text{O}^+(\text{CH}_2)_3\cdot\text{BF}_3\text{OH}^-$  on monomer.

*R-H substitution reactions.*—Emmons & Hawthorne (45) have observed a 20 per cent secondary H-D isotope effect in the acetate-induced bromination of cyclopentyl-2,2,5,5- $\text{H}_4^2$  phenyl ketone and have interpreted this result as indicating the enol form (rather than the enolate ion) is produced directly in the rate-determining step as proposed by Swain (46). The argument is based on the finding of a similar secondary isotope effect in the acid-catalyzed bromination of cyclopentyl phenyl ketone where the enol is surely the first reaction product and the assumptions, (a) that the secondary isotope effect is a measure of hyperconjugative stabilization of the enol double bond, and (b) that the enolate anion would not be stabilized by hyperconjugation. The second assumption is in contrast to the postulates of Seubold (47). Irrespective of the validity of the assumptions, it appears reasonable to question the structural assignment for the starting material which was prepared by a sequence involving as one step the conversion of cyclopentanol-2,2,5,5- $\text{H}_4^2$  to the corresponding chloride. Loftfield (48) has noted 20 per cent of  $\text{C}^{14}$ -isotope-position rearrangement in the analogous reaction of cyclopentanol-1- $\text{C}^{14}$  with phosphorus tribromide and a similar rearrangement might have led to the formation of some  $\alpha$ -deuterocyclopentyl phenyl ketone.

Doering *et al.* (49, 50) have studied the photochemically induced reactions of ethyl diazoacetate and diazomethane with saturated hydrocarbons. The hydrocarbon was used as the solvent in each case. Attack on the carbon-hydrogen bonds resulted with formation of  $\text{R}-\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$  or  $\text{R}-\text{CH}_3$ . With ethyl diazoacetate, a slight preference was noted for attack at *tert*-hydrogens. However, with diazomethane, virtually random introduction of  $\text{CH}_2$  groups was found. Doering & LaFlamme (51) report both *trans*-2-pentene and 2-methyl-2-butene among the products from irradiation of diazomethane in *trans*-2-butene. These reactions have been interpreted as involving  $\text{CH}_2$  "radicals." The pronounced lack of discrimination in attack on various kinds of R-H bonds suggests that the reaction which destroys  $\text{CH}_2$  must be extremely fast. If the initial step is hydrogen abstraction, two radicals will be formed in a solvent cage with paired or unpaired spins of the

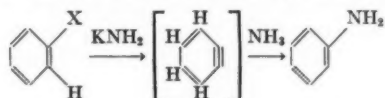
odd electrons depending on whether the  $\text{CH}_2$  intermediate was in a singlet or triplet state.



If the electrons are unpaired, a change in electron multiplicity must occur before the  $\text{R}-\text{CH}_3$  bond can be formed. Since it has not been established that such changes in multiplicity are necessarily slow compared to radical diffusion from the solvent cage, the production of  $\text{RCH}_3$  without serious competitive formation of  $\text{R}-\text{R}$  and  $\text{CH}_3-\text{CH}_3$ , or even allylic rearrangement with *trans*-2-butene to yield 3-methyl-1-butene, does not necessarily prove anything with regard to the state of  $\text{CH}_2$ . The intermediate in the photochemical reactions of aliphatic diazo compounds with hydrocarbons may well be in an excited state since the copper-induced reaction of ethyl diazoacetate in cyclohexane affords only diethyl fumarate.

#### NUCLEOPHILIC SUBSTITUTION AT UNSATURATED CARBON ATOMS

*Rearrangements in nucleophilic substitution reactions of aryl or vinyl derivatives.*—It was first proposed, on the basis of  $\text{C}^{14}$ -tracer studies with labeled chlorobenzene, that the unusual rearrangements discovered by Gilman *et al.* (52, 53, 54) which often occur in the amination of aromatic halides with metallic amides in liquid ammonia or ether involve elimination-addition mechanisms by way of a "benzyne" intermediate [Roberts *et al.* (55)]. Considerable evidence in support of this mechanism has been offered from additional  $\text{C}^{14}$ -tracer studies, kinetic hydrogen isotope effects and



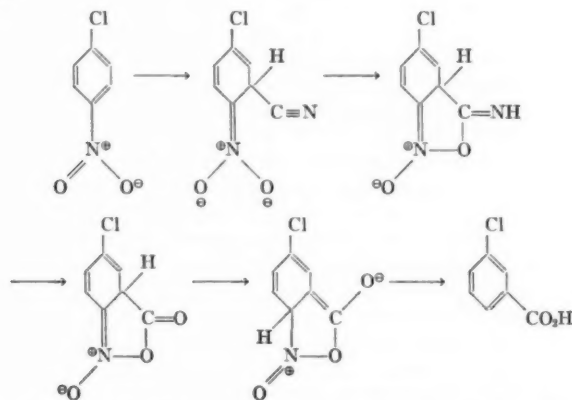
substituent effects on the orientation in amination of substituted halo-benzenes [Roberts *et al.* (56, 57)]. Consideration of the relative reactivities of the halo-benzenes and the kinetic isotope effect observed when the hydrogen next to the halogen was substituted with deuterium indicated the operation of a stepwise dehydrohalogenation with chlorobenzene and a concerted dehydrohalogenation with bromo- and iodobenzenes. A number of other possible mechanisms were shown to be inconsistent with the experimental facts. Strong evidence for the postulated intermediate is provided by the fact that it may be trapped with a variety of reagents when generated under the reaction conditions or in other ways [Roberts *et al.* (56); Wittig & Pohmer (58); Wittig & Ludwig (59); Leake & Levine (60)].

This type of mechanism for displacement reactions of aryl halides appears to be applicable to a variety of situations. The coupling of 1- and 2-fluoronaphthalenes with phenyllithium affords identical mixtures of 1- and 2-phenylnaphthalenes (1:2) [Huisgen & Rist (61, 62)]. The expected intermediate formation of 1- and 2-phenylnaphthyllithium derivatives was demonstrated. A similar mechanism was postulated by Jenny & Roberts

(63) for the coupling of phenyllithium with fluorobenzene. Bunnett & Brotherton (64) have shown that elimination-addition suffices to account for the amination of bromonaphthalenes with piperidine and sodium amide. The hydrolysis of halobenzenes and halotoluenes with 4 *M* sodium hydroxide at 340° give rearrangement products which indicate the operation of the benzyne mechanism. [Roberts, Bottini & Semenow (65); Bottini & Roberts (66)]. The utility of the benzyne intermediate in accounting for the variety of side products observed in the high-temperature alkaline hydrolysis of chlorobenzene has been demonstrated by Lüttringhaus & Ambros (67). An alternative "1,3-addition" mechanism for amination-rearrangement reactions of aryl halides has been offered by Morton (68) which, as presented, fails to account adequately for the experimental facts.

The balance between the operation of the elimination-addition and normal (nonrearranging) bimolecular type substitution mechanisms has been investigated to some degree (64, 66). Generally, it appears that those factors which determine the ratios between elimination and substitution in the reactions of alkyl halides are significant. Thus, strong bases, high temperatures and low polarizability of the leaving group favor elimination (66).

*The von Richter reaction.*—The conversion of *p*-nitrochlorobenzene by potassium cyanide in ethanol to *m*-chlorobenzoic acid ostensibly appears to be related to the nucleophilic substitution reactions discussed above but has been shown by Bunnett & Rauhut (69) to involve an addition-elimination mechanism. In the reaction with *p*-nitrochlorobenzene, it was shown that neither *m*-chlorobenzonitrile nor *m*-chlorobenzamide could be an intermediate in the formation of *m*-chlorobenzoic acid. As a result, the mechanism proposed earlier (70) has been modified to include the following key intermediates.

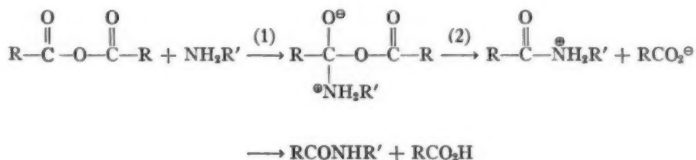


*Haloethylenes with thiols and sulfite.*—Elimination-addition mechanisms have been demonstrated by Truce *et al.* (71, 72) in the base-catalyzed displacement of halogen from dichloroethylenes by thiols and sulfite. Kinetic

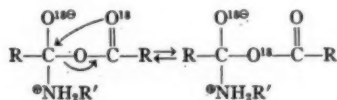
and chemical evidence was adduced for chloroacetylene as the initial reactive intermediate. Rearrangement, as expected, was observed with vinylidene chloride which gave the same 1,2-disulfide with thiols as obtained with *cis*-dichloroethylene. Also as expected for the postulated mechanism, was the finding that *cis*-dichloroethylene reacts more readily than the *trans*-isomer.

**Iodonium compounds.**—Beringer *et al.* (73) have made a thorough kinetic study of the reaction of diphenyliodonium ions with chloride ion in competition with solvolysis in hydroxylic solvents. The chloride ion reaction appears to involve a first-order decomposition of a chloride ion-iodonium ion complex (presumably the ion pair). The solvolysis rate is strongly repressed by added potassium chloride and hence appears to take place by attack of hydroxylic solvent on the free cation. Copper (I) has a potent catalytic effect on the reaction with chloride ion.

**Acyl derivatives.**—The reaction between anhydride and amines has been characterized as a multiple-step process as follows by Denney & Greenbaum (74).



With the aid of carbonyl-labeled  $\text{O}^{18}$ -benzoic anhydride, step 2 in the above sequence has been shown to be substantially irreversible in liquid ammonia since just half of the  $\text{O}^{18}$  appears in the carbonyl group of the benzamide. On the other hand, the labeled anhydride reacts with aniline in ether to give benzanilide containing but 33 per cent of the  $\text{O}^{18}$ . This result indicates the oxygens have become randomized during the reaction as expected if step 2 were reversible. Taken at face value, this leads to the surprising conclusion that the rate-determining step is the proton transfer from the rather strong acid  $\text{RCONH}_2\text{R}'$  to benzoate ion. Equilibration by way of exchange involving the benzoic acid formed initially in the reaction and converted to benzoate ion by aniline was shown to be too slow to account for the results with the aid of added  $\text{C}^{14}$ -labeled benzoic acid which gave much less than the statistical amount of  $\text{C}^{14}$ -containing benzanilide. It is possible that the equilibration might take place through rapid isomerization of the product of reaction 1 as follows.



If reaction 1 is also reversible this would lead to a statistical distribution of  $\text{O}^{18}$ -label.

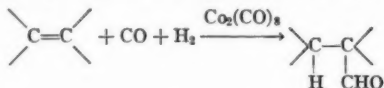
## ADDITIONS TO MULTIPLE BONDS

**Carbon-carbon multiple bonds; polymerization.**—Szwarc, Levy & Milkovich (75) have shown that the polymerization of styrene initiated by complexes of sodium with aromatic hydrocarbons [Scott (76)] behaves as though a styrene negative radical ion were formed which dimerizes and gives a chain growing on each end by successive carbanion additions. The growing chain ends are quite stable "living polymers" and the rate and over-all extent of growth can be regulated by the styrene concentrations. Block polymers have been reported as the result of adding different monomers to "living" ends [(Szwarc & Rembaum (77)). Szwarc *et al.* (78) have found trifluoroacetic acid to be an extremely effective catalyst for polymerization of styrene. The degree of polymerization depends markedly on whether trifluoroacetic acid or styrene is in excess. Long-chain polymer is formed when styrene is added to the acid and short-chain polymer is formed by the reverse addition of the acid dissolved in ethylbenzene to styrene. The difference in behavior is attributed to the difference in anion environment, after a proton has been transferred to the styrene double bond. In trifluoroacetic acid, the anion is presumed to be so stabilized by other trifluoroacetic acid molecules as to be relatively ineffective at chain termination while the reverse is presumed true in styrene as a solvent.

**Thiols.**—Truce & Simms (79) have demonstrated that arylthiolate salts in alcohol solutions add to substituted acetylenes such as phenylacetylene to give vinyl sulfides with quite clean *trans*-stereochemistry. This result can be accounted for with a configurationally stable intermediate vinyl sulfide carbanion or a concerted *trans*-addition reaction. Similar stereochemical results have been obtained by Miller (80, 81) in the base-induced addition of methanol to phenylacetylene. In this case, the addition is first-order in acetylene and first-order in methoxide; it is also kinetically independent of the methanol concentration which suggests a rate-determining addition to yield a configurationally stable carbanion or the equivalent (81).

**Michael addition.**—Kamlet & Glover (82) have made the first thorough study of the kinetics of a Michael-type addition using  $\beta$ -nitrostyrene and barbituric acid. Strong evidence was obtained for a rate-determining addition of barbiturate anion to  $\beta$ -nitrostyrene followed by a fast proton transfer.

**Hydroformylation.**—The rates of hydroformylation of alkenes with carbon monoxide and hydrogen in the presence of dicobalt octacarbonyl have been measured by Wender *et al.* (83). Previous work (84, 85)



indicated initial formation of an alkene-cobalt carbonyl complex. The relative rates with various alkenes were consistent with a substantial steric effect on complex formation.

**Hydration.**—Purlee & Taft (86) have studied the effect of deuterium in

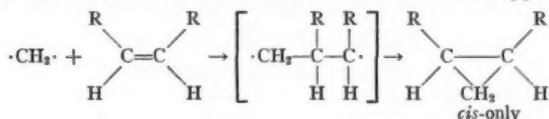


the solvent on the aqueous acid-catalyzed rates of hydration of trimethyl-ethylene and methylcyclopentene. The rate variation with fraction of deuterium in the solvent followed the theoretical curve calculated by the method of Butler and provides evidence for a rapid pre-equilibrium involving a proton transfer to the alkene to yield what might be formulated as a  $\pi$ -complex.

**Hypochlorous acids.**—Addition of hypochlorous acid to isobutene has been shown to give 1-chloro-2-methyl-2-propanol and 3-chloro-2-methylpropene as the principal alkenic side product [de la Mare & Salama (87)]. This chloro-alkene is also the principal E1 product from the hydrolysis of 1,2-dichloro-2-methylpropane and it has been suggested that a common intermediate, the 1-chloro-2-methyl-2-propyl carbocation, is involved in both addition and solvolysis.

**Carbanions.**—Hart (88) has shown that the addition of arylalkanes (at the position  $\alpha$ - to the ring) to ethylene in the presence of alkali metal or alkali metal hydrides most probably involves aryl alkyl carbanion intermediates by using deuterium as a tracer for hydrogen exchange reactions and optically-active 2-phenylpentane as the arylalkane. Similar studies have been reported by Mark & Pines (89).

**Carbenes.**—Skell & Garner (90), Skell & Woodworth (91), and Doering & La Flamme (51) have observed that the cyclopropane-forming additions of dibromomethylene and methylene to alkenes occur exclusively in the *cis*-manner. This has been interpreted (90, 91) as indicating the addends to be present in singlet states which are capable of bonding simultaneously to both carbon atoms in the transition state. If attack were by triplet methylene it is assumed that attack could only occur at one end of the double bond and a diradical would be formed. This diradical would have the opportunity of



undergoing stereochemical equilibration before ring closure, provided rotation about the single bond could occur faster than the electron multiplicity change required for closure of the three-membered ring (cf. p. 306). Skell & Garner (92) have been able to set up a scale of reactivities for alkenes with dibromomethylene by competition experiments. This reactivity scale can be correlated much more satisfactorily with reactivities in bromine addition and epoxidation than with reactivities toward trichloromethyl radicals.

The reaction of ketene with  $\text{C}^{14}$ -diazomethane has been shown to afford a mixture of one-fourth cyclobutanone-3- $\text{C}^{14}$  and three-fourths cyclobutanone-2- $\text{C}^{14}$  as expected if intermediate formation of cyclopropanone or an entity with similar symmetry properties were involved [Semenow, Cox & Roberts (93)].

**Diels-Alder additions.**—Berson *et al.* (94) have shown that the conversion of the *endo*-cyclopentadiene-maleic anhydride adduct labeled with  $\text{C}^{14}$  in

the carbonyl carbons to the *exo*-isomer in the presence of inactive maleic anhydride leads to more radioactive product than could be accounted for by exclusive operation of a simple dissociation-recombination process. A complex or solvent-caged aggregate was postulated as the interconversion intermediate.

*Free radical additions.*—The steric course of free radical addition to 1-bromocyclohexene has been further investigated by Goering, Relyea & Larsen (95). The degree of stereospecificity in the additions decreased in the order  $C_6H_5SH > H_2S > HSCH_2CO_2H$  although all three reagents give predominant *trans*-addition. Stereospecificity increases with increasing concentration of the addend. The authors point out that all observations are consistent with the view that stereochemical equilibration of the first-formed radical is slow, allowing some molecules to abstract hydrogen from an addend molecule while the radical retains its original conformation in which the newly added group is, presumably, axial.

Several papers dealing with the Meerwein and Sandmeyer reactions have appeared and the diversity of mechanistic suggestions leaves one in a quandary as to proper classification. Kochi (96) has concluded on the basis of a large array of rate data that both reactions are catalyzed by cuprous halide but not by cupric halide. At high  $Cl^0/Cu(I)$  ratios, the initiator is rendered inactive by conversion to high halide complexes such as  $CuX_3^{2+}$ . Under these conditions, added alkene accelerates the reaction but, with low  $Cl^0/Cu(I)$  ratios, the rate of decomposition of diazonium ion is independent of the alkene concentration although the ratio of Sandmeyer/Meerwein products is controlled by the alkene level. The author is reserved in specifying mechanistic timing but prefers some sort of radical process in which catalyst, diazonium ions and, perhaps alkene, generate a radical which is subsequently destroyed in an efficient chain transfer reaction with cupric halide. The feasibility of the last step is established by the observation (97) that phenyl radicals, generated in several different ways, add to styrene and acrylonitrile to give derived radicals which are, in turn, smoothly converted to halides by cupric or ferric halides dissolved in the medium.

Vogl & Rondestvedt (98) found that the Meerwein reaction resulted in nonstereospecific addition to the methyl and ethyl esters and nitriles of maleic and fumaric acid. They maintain that the reaction involves a complex of cupric chloride, diazonium chloride and alkene. In their picture, the steric memory of the alkene portion of a highly organized complex is lost at a stage when the alkene has been converted to a cationic radical. The ultimate production of a cationic center adjacent to a nitrile or carboxyl function is not appealing. In view of Kochi's results, it is hard to see how one can hold that cupric copper is generally an active catalyst.

#### ELIMINATION REACTIONS

*Bimolecular elimination.*—The stereochemistry of the E2 reaction has been examined in a number of specially designed systems. Cristol *et al.* (99)

found that *trans*-elimination of hydrogen chloride from *cis*-1,2-dichloroacenaphthene occurs about 740 times as fast as *cis*-elimination from the *trans*-isomer (sodium hydroxide in ethanol). The authors conclude from this fact and a comparison of the absolute rate of reaction of the *cis*-isomer with that of other systems that the *trans*-elimination occurs in one stage, and that the *cis*-elimination occurs in two stages with intervention of a phenyl-stabilized carbanion. Weinstock, Pearson & Bordwell (100) studied the rates of elimination of *p*-toluenesulfonic acid from the *cis*- and *trans*-isomers of 2-*p*-tolylsulfonylcyclohexyl and 2-*p*-tolylsulfonylcyclopentyl *p*-toluenesulfonates. In all cases, the proton was lost from the carbon carrying the sulfone group. With hydroxide ion in 50 per cent dioxane in the cyclohexyl system,  $k_{E2-trans}/k_{E2-cis} = 434$ , and for the cyclopentyl system,  $k_{E2-trans}/k_{E2-cis} \cong 20$ . Since the reactions are subject to general base catalysis, the authors conclude both *cis* and *trans* E2-eliminations in these systems are one stage, the enhanced acidity of the proton lost accounting for the relatively small factors favoring *trans* elimination. Winstein *et al.* (101) studied the second-order rates of reaction of nucleophiles with *cis*- and *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonate. In the latter system, the leaving group must occupy an equatorial position, and over-all *cis*-elimination must compete with substitution. With this isomer,  $\text{NaI} \cong \text{LiBr} = 5\text{LiCl}$  in rate, while the fraction of the rate involving over-all *cis*-elimination (substitution competed) passed from 0.30 to 0.25 to 0.10 for the three nucleophiles. These results were interpreted in terms of the intermediate formation of an anion-solvated ion-pair. The ion-pair then partitions between substitution and elimination, depending on the nucleophilicity vs. basicity of the two anions flanking the carbonium ion.

In a study of eclipsing effects in the E2 reaction, Cram *et al.* (102) studied the relative rates of the E2 reaction of the two diastereomers of 1,2-diphenyl-1-propyl-X. The diastereomeric starting materials were of about equal stability, whereas equilibration of the olefinic products demonstrated *trans*- $\alpha$ -methylstilbene to dominate over the *cis*-isomer by a factor of 50. Clean *trans*-elimination occurred in all cases except where  $\text{X} = (\text{CH}_3)_3\text{N}$ , and the medium was *t*-BuOH-*t*-BuOK, in which the *erythro*-isomer underwent a *cis*-elimination. The value of the rate ratio,  $k_{E2-threo}/k_{E2-erythro}$ , was used as a measure of the extent of eclipsing of the systems in the transition state. With  $\text{X} = \text{Br}, \text{Cl}$  and  $\text{N}(\text{CH}_3)_3$  in  $\text{C}_2\text{H}_5\text{OH}-\text{C}_2\text{H}_5\text{ONa}$  the ratios were 0.7, 1.1, and 57, respectively, whereas in  $(\text{CH}_3)_3\text{COH}-(\text{CH}_3)_3\text{COK}$ , the ratios were 5.4, 15, and 1.1, respectively. The results were interpreted in terms of a transition state whose geometry could be varied from that similar to a simple ionization of  $\text{C}_x-\text{X}$ , through one involving considerable carbon-carbon double bond character, to one with the  $\text{C}\beta-\text{H}$  bond largely broken and the other bonds largely intact.

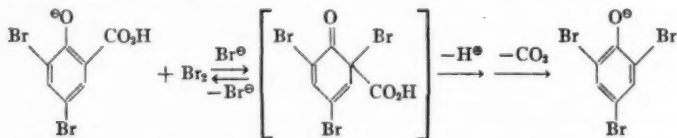
Brown *et al.* (103) demonstrated in a series of papers that steric strains in E2 transition states increase with increasing steric requirements of (a) the substituents attached to the incipient double bond, (b) the attacking base,

and (c) the leaving group. The operation of the Saytzeff rule which predicts the most highly substituted olefin as product is interpreted as due to electronic effects, whereas the operation of the Hofmann rule which predicts the least highly substituted olefin is considered due to steric effects. An extensive body of data correlates with the above conclusions. Cristol *et al.* (104) found that *cis*- and *trans*-2-bromo-1-cyclohexyl nitrates and arene-sulfonates undergo elimination with iodide ion by kinetics which could best be interpreted in terms of: 1) a preferred *trans*-elimination; 2) an  $S_N2$  reaction followed by a *trans*-elimination in systems where *trans*-elimination cannot occur directly, or where substitution is much faster than elimination.

Rondestvedt & Rowley (105) have determined the activation parameters, solvent and salt effects and the influence of structural changes on rates of base-catalyzed cleavages of  $\alpha,\beta$ -diaryl- $\beta$ -alkyl- $\beta$ -hydroxypropionic acids. The experimental data are in accord with the step-wise mechanism previously proposed for the dealdolization of diacetone alcohol despite the statement of the authors that a "concerted" removal of hydroxyl hydrogen and carbon-carbon bond cleavage is more likely. Each formulation involves essentially identical changes of configuration between ground and transition states and the stepwise mechanism avoids the difficulty of having to suppose that either the proton transfer is indeed rate-determining or that the conjugate base of the hydroxypropionate fails to undergo cleavage.

Weinstock (106) has shown that the pyrolysis of  $\alpha$ -bromoesters to yield alkyl bromides and  $\alpha$ -lactones proceeds with complete inversion of configuration at the carbon carrying the bromine and occurs readily with ethyl *trans*-2-bromocyclopentaneacetate but only very slowly with the corresponding *cis*-isomer. A two-stage ionic mechanism fits the experimental data most satisfactorily.

*Decarboxylation and decarbonylation.*—The brominative decarboxylations of salicyclic and *p*-hydroxybenzoic acids have been elegantly studied by Grovenstein & Henderson (107). Attention was focused on the last step of the reactions, the attack of bromine on the dibromosalicylic or dibromo-*p*-hydroxybenzoic acids. A mechanism was inferred from the kinetics which in the presence of bromide ion, involves reversible formation of tribromocyclohexadienonecarboxylic acid and a rate-controlling decarboxylation of the salt of this substance.



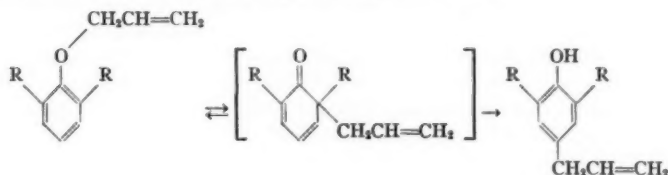
The  $C^{12}$ - $C^{13}$  kinetic isotope fractionation factor has been used to verify the above mechanism (108). The ratio  $k_{12}/k_{13}$  was found to be  $1.002 \pm 0.003$  in the absence of added bromide ion and 1.045 in the presence of 0.300 *M* hydrogen bromide. Under the latter conditions, the first step is rate-deter-

mining (no back reaction from cyclohexadienone intermediate) so no isotopic fractionation is to be expected.

Banholzer & Schmid (109) have studied the acid-catalyzed decarbonylation of benzoylformic acid. The carbon monoxide was shown to be formed exclusively from the carboxyl group with the aid of  $C^{14}$  as a tracer. As in other cases (110, 111, 112), it appears that acyl functions "migrate" more readily than do aryl or alkyl functions under influence of acids or basic reagents.

#### REARRANGEMENTS AND ISOMERIZATIONS

*The para-Claisen aryl alkyl ether rearrangement.*—Since the demonstration by Rhoads *et al.* (113) that the experimental basis for the formulation of the *para*-Claisen rearrangement of 2,6-substituted allyl phenyl ethers as either a free-radical or a  $\pi$ -complex mechanism was incorrect, considerable evidence has been obtained for a "double cyclic" process involving a cyclohexadienone intermediate as suggested by Hurd (114).



Schmid & Schmid (115) and Ryan & O'Connor (116) have shown with the aid of  $C^{14}$  that the allyl group is attached at the *para*-position by the same  $CH_2$ -group as in the ether. The tracer technique also demonstrated the reaction to be clearly intramolecular (115). Curtin & Johnson (117) and Schmid *et al.* (118, 119) have demonstrated that, if R— is an allylic group, at some intermediate stage it becomes equivalent to the migrating allyl group. The first step of the reaction has been shown to be reversible if R— is an allylic group (117, 119). Conroy & Firestone (120) have trapped the dienone intermediate with maleic anhydride. Curtin & Crawford (121) have synthesized such dienones and shown they have the proper characteristics to be reaction intermediates at high temperatures.

*Wagner-Meerwein rearrangements.*—Schaeffer & Collins (122) have investigated the products of the phosphoric acid dehydration of *cis*- and *trans*-2-phenylcyclohexanol-2- $C^{14}$ . The *cis*- and *trans*-isomers gave 88 per cent and 21 per cent of 1-phenylcyclohexene, respectively. Phenyl migration occurred during the dehydration of the *trans*-alcohol.

Rylander & Meyerson (123) have studied the ionization under electron impact in a mass spectrometer of labeled *t*-butylbenzene and 3-ethyl-3-phenylpentane, and their unlabeled counterparts. The results are correlated on the basis of the formation of cyclopropane rings coordinated with phenyl, methyl or hydrogen cations.

*The solvolytic deamination reaction.*—Cannell & Taft (124) found the deamination of isobutylamine with nitrous acid in aqueous solution to give products of both methyl and hydrogen rearrangement. No detectable exchange of hydrogen was associated with the hydrogen migration to give *t*-butyl alcohol when the reaction was carried out in D<sub>2</sub>O. The hydrogen migration is considered to pass through a bridged protonium ion, a species different from the  $\pi$ -complex (protonated double bond) which is considered by the authors to be an intermediate in the hydration of isobutene.

The deamination in aqueous nitrous acid of 1,2,2-triphenylethylamine, alternatively labeled with radioactive carbon at carbon 1 and in the 1-phenyl nucleus, has been studied by Bonner & Collins (125). The distribution of C<sup>14</sup> in the 1,2,2-triphenylethanol product can be most simply explained on the basis of the equilibration of planar, benzyl cations as intermediates.

Huisgen & Reimlinger (126) studied the kinetics and mechanism of the rearrangement of *N*-nitrosoacylalkyl (aryl) amines to, first, the diazo ester (slow step) followed by the loss of nitrogen to give stable products (fast step). The rates of evolution of nitrogen were measured, and substituent effects indicate that steric factors outweigh polar influences in this reaction. The final products are carboxylic esters, and alkenes when the alkyl group of the starting materials are secondary. Evidence was obtained for the intervention of carbonium ions solvated by either the leaving ester anion, solvent molecules, or added solute molecules.

*Pinacol rearrangement.*—Benjamin & Collins (127) have studied the rearrangement of diphenyl-*p*-tolylacetaldehyde-1-C<sup>14</sup>, of 1,2-diphenyl-1-*p*-tolylethylene glycol (labeled at C-1, C-2, and in the nucleus of the phenyl at C-1) and of 1,1-diphenyl-2-*p*-tolylethylene-2-C<sup>14</sup> glycol in sulfuric acid and formic acid. All three compounds lead to mixtures of *p*-tolyldeoxybenzoin and benzhydryl *p*-tolyl ketone. The intermediate common to these rearrangements appears to be the conjugate acid of diphenyl-*p*-tolylacetaldehyde. The double-labeling technique allowed phenyl/*p*-tolyl migration ratios to be estimated.

*Transannular rearrangements.*—Hydroxylation of cyclohexene with performic acid has been demonstrated by Cope *et al.* (128) to give *trans*-1,4-cyclohexanediol (0.03 per cent) and the two stereoisomeric 2,2'-dihydroxydicyclohexyl ethers in addition to *trans*-1,2-cyclohexanediol. Ethanolysis of the *p*-toluenesulfonate of 6-ketocyclodecanol was found by Goering *et al.* (129) to give a mixture of *cis*- and *trans*-[5.3.0] bicyclodecan-2-one. The reaction was demonstrated to proceed through an acid-catalyzed enolization (rate determining), followed by transannular participation of the double bond in ionization of the sulfonate ester. Prelog & Kung (130) observed a transannular pinacol rearrangement with 1-methyl-1,6-cyclodecandiol which when treated with acid gave 6-methyl-1-cyclodecanone. An experiment with a deuterium label demonstrated occurrence of a transannular hydride shift. 1,6-Dimethyl-1,6-cyclodecandiol with acid gave an unsaturated hydrocarbon.

A 1,5-phenyl migration was observed by Letsinger & Lansbury (131) when 8-benzhydryl-1-naphthoic acid was treated with aluminum chloride.

The product, a cyclic hemiketal of 1-benzoyl-8-( $\alpha$ -hydroxybenzyl)-naphthalene, was presumed to have arisen through a phenonium ion bridge.

In an open-chain system, Winstein *et al.* (132) have demonstrated aryl participation in ionization of certain 4-aryl-1-butyl and 5-aryl-1-pentyl *p*-toluenesulfonates, ring-closed products resulting. In some butyl systems, "tetramethylene phenonium ions" were demonstrated to intervene as reaction intermediates.

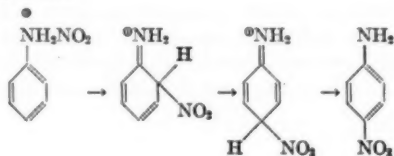
In a study of the "*i*-cholesterol" rearrangement, Kosower & Winstein (133) have prepared and solvolyzed both diastereomeric 3,5-cyclocholestan-6-yl trichloroacetates, and 3,5-cyclocholestan-6- $\beta$ -yl chloride. The first two compounds as well as cholesteryl toluenesulfonate in methanol-chloroform yield 90 per cent 3,5-cyclocholestan-6- $\beta$ -yl and 10 per cent cholesteryl methyl ethers. A common homoallylic hybrid carbonium ion intervenes in these solvolyses.

*The S<sub>N</sub>2' reaction.*—The steric course of the S<sub>N</sub>2' reaction has been examined by Stork & White (134). The reaction of *trans*-6-alkyl-2-cyclohexen-1-yl 2,6-dichlorobenzoates with piperidine or sodium di-*n*-butylmalonate afforded *trans*-4-alkyl-2-cyclohexen-1-yl derivatives by kinetically second-order processes. Clearly, the entering group approaches on the same side of the ring as the leaving group is located.

*Mechanism of the Fries rearrangement.*—Evans *et al.* (135) have studied the kinetics and mechanism of the Fries rearrangement of *o*-tolyl acetate with titanium tetrachloride in homogeneous nitrobenzene solution. A complex involving two moles of titanium tetrachloride and one of ester seems to form and subsequently rearranges, partly intramolecularly, to give 3-methyl-4-hydroxyacetophenone.

*The benzidine and related rearrangements.*—Shine (136) has studied the thermal rearrangement of 2,2'-hydrazonaphthalene to 2,2'-diamino-1,1'-binaphthyl. As was reported by Krolik & Lukashevich (137) the reaction is not catalyzed by base as was long believed. The rate is highest in more acidic solvents, being 34 times faster in methanol than in acetone. The addition of pyridine in gross amount (1.25 *M*) decreases the rate in methanol by 35 per cent. The magnitude of these effects seems to be more nearly consonant with a mild catalysis of a radical reaction than with an acid-catalyzed process.

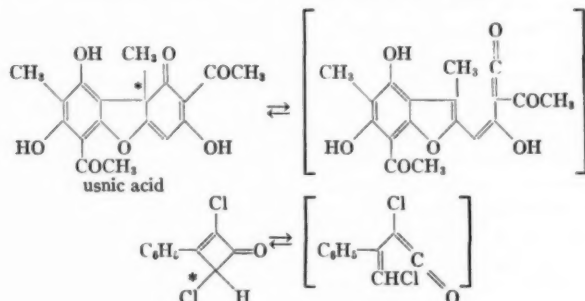
Brownstein, Bunton & Hughes (138) found that the acid-catalyzed rearrangement of phenylnitramine to *p*-nitroaniline occurs without exchange with N<sup>15</sup>-labeled nitrate in the reaction medium. They suggest a stepwise process and further advocate consideration of a similar mechanism for the benzidine rearrangement.





**Benzilic acid rearrangement.**—Doering & Urban (139) have shown that potassium *t*-butylate will cause a highly effective rearrangement of benzil to *t*-butyl benzilate. Thus, hydroxide ion is not a specific catalyst for the benzilic acid-type rearrangement and no intramolecular proton transfer is required in the rate-determining step. Pfeil *et al.* (140) have found that the rates of benzilic rearrangement of 2,2'-dichlorobenzil are markedly dependent on the nature of the metal hydroxide. Even with 0.01 *N* solutions in 1:1 dioxane-water, the rate with TlOH was almost 85 times greater than with KOH. The thallium hydroxide-induced reactions were found to be much more powerfully influenced by neutral salt and solvent changes than the alkali-hydroxide-induced reactions. Apparently, the metal cation plays an important part in governing the stability of the hydroxide-benzil complex (141) and its subsequent rate of rearrangement.

**"Valence tautomerism" reactions.**—Two unusual and seemingly unrelated thermal racemization reactions have been suggested to have essentially identical mechanisms involving ring-opening and ring-closing. The racemizations of optically active usnic acid [Stork (142)] and 2,4-dichloro-3-phenylcyclobutenone [Jenny & Roberts (143)] occur at saturated carbons (here marked with asterisks). With each compound, ring opening



to a vinylketene intermediate would destroy the center of optical asymmetry and ring closure would then yield the racemic product. With the dichlorophenylcyclobutenone, it was shown by kinetic and tracer studies that neither the C—Cl or C—H bonds were broken in the racemization process. Furthermore, it was possible to trap the ketene intermediate with ethanol or acetate ion.

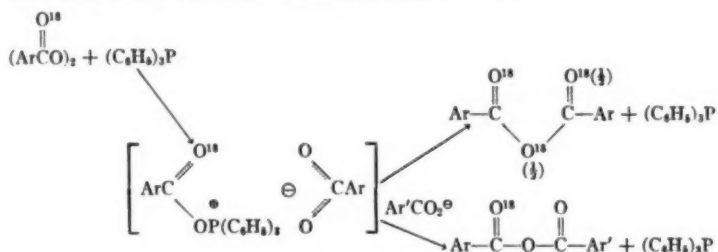
**Miscellaneous.**—Tarbell & Lovett (144) have investigated the base-induced isomerization of allyl *n*-hexyl sulfide to propenyl *n*-hexyl sulfide. The rate of isomerization of the corresponding allyl *n*-hexyl ether was negligible under the same conditions. Isomerization in deuterioethanol and product analysis for deuterium indicated reversible formation of a carbanion intermediate since much product was obtained containing two deuteriums.

Propenyl *n*-hexyl sulfide exchanged too slowly to account for the observed H—D exchange.

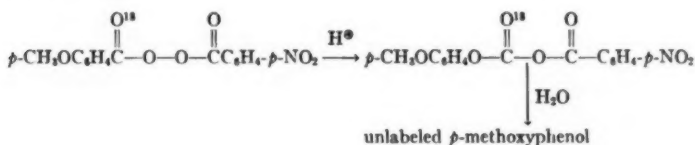
The kinetics of the mutarotation of glucose have been studied with the aid of a polarographic method by Los, Simpson & Wiesner (145). General base-catalysis was confirmed for phosphates and the concentration of free aldehyde was calculated to be 0.0026 per cent of the glucose present.

The kinetics of the quantitative thermal Schonberg rearrangement of bis-(4-chlorophenyl)-thioncarbonate to the thiolcarbonate have been shown to be strictly first-order and a four-membered cyclic transition state seems required [Powers & Tarbell (146)].

Greenbaum, Denney & Hoffmann (147) found that the reaction of triphenylphosphine with benzoyl peroxide gives benzoic anhydride in which one isotopically labeled carbonyl oxygen has become randomized. An ion-pair mechanism is proposed and experimentally fortified by the observation that *p*-nitrobenzoate ion added to the reaction mixture is extensively incorporated in the product. Suitable controls were run.



Using a carbonyl-labeled, unsymmetrical peroxide, Denney (148) showed that no randomization occurs in the acid-catalyzed rearrangement to aryl acyl carbonate.

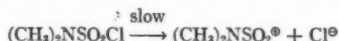


#### MISCELLANEOUS POLAR REACTIONS

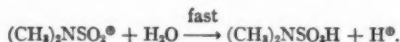
Winstein & Traylor (149) have shown that the C—Hg bonds of bridge-head mercury compounds react normally in several free-radical and electrophilic substitution reactions. This behavior is in marked contrast to the extraordinarily low reactivity of the corresponding halogen compounds in nucleophilic reactions (150). It seems reasonable to conclude that the intermediates involved in free radical or electrophilic substitutions of the type

investigated do not seem to have any marked preference for a planar carbon at the site of substitution.

Evidence has been presented by Hall (151) that dimethylsulfamyl chloride hydrolyzes in water solution by a two-stage ionization process,



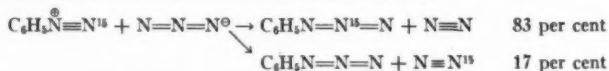
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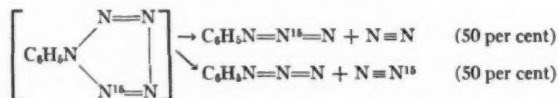
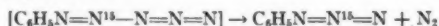
Piperidine has no effect on the over-all rate of chloride ion formation but, in the presence of piperidine, the reaction product is dimethylsulfamylpiperide. Alkylsulfonyl chlorides appear to react by a one-stage process.

Havinga, de Jongh & Dorst (152) have reported a remarkable pH-sensitive, temperature-independent photochemical acceleration of the hydrolysis of nitrophenyl phosphates. The *meta*-derivative is some 30 times more sensitive to photochemical acceleration than the *ortho*- or *para*-isomers. The *meta*-substituted phosphate reacts particularly rapidly at high pH values. The sulfates behave similarly, except no pH dependence was noted. Nucleophilic attack of hydroxide on a photochemically excited nitrophenyl ring was postulated although it was not made clear how this would give greater acceleration with the *meta*-derivatives in the absence of rearrangement reactions. It is not known whether these hydrolyses proceed with C—O or P—O cleavage.

Ugi *et al.* (153) have reported an elegant series of experiments which delineate the manner in which phenyldiazonium chloride reacts with azide ion to yield phenylazide and nitrogen. At 0° in water, phenyldiazonium chloride labeled with N<sup>15</sup> at the end nitrogen yields 83 per cent of N<sup>15</sup>-labeled phenylazide and 17 per cent labeled nitrogen (154).



This isotopic distribution has been formulated (155, 156) as the possible result of concomitant formation and decomposition of a phenylpentazene and a phenylpentazole.

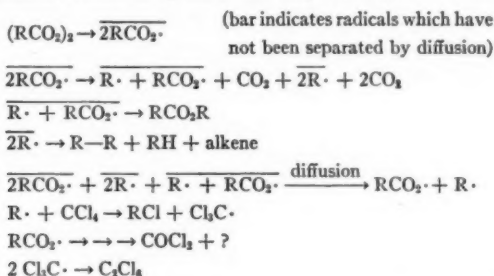


The reaction of benzenediazonium chloride with lithium azide in methanol at -50° gives a rapid first-order evolution of 75 per cent of the theoretical amount of nitrogen. At higher temperatures the balance of the nitrogen is liberated in a subsequent, first-order reaction. The proportions of these two reactions corrected to water solution correspond approximately to the

proportions of phenylpentazole intermediate which might be calculated to be present from the amount of  $N_2^{15}$  formed in the tracer experiment (156, 157). Investigation (153) of the two-stage decomposition with  $N^{15}$ -labeled phenyldiazonium chloride reveals that the initial rapid evolution of nitrogen results in formation of gas with no excess  $N^{15}$  while the slow secondary reaction gives the calculated  $N^{15}$  content expected for the phenylpentazole intermediate.

#### MISCELLANEOUS FREE RADICAL REACTIONS

*Peroxide decomposition.*—The decomposition of diacylperoxides continues to consume many man-years of research. DeTar & Weis (158) made a very thorough product analysis of the decomposition of  $\delta$ -phenylvaleryl peroxide in very dilute solutions where induced reactions were negligible, as evidenced by the invariance of the carbon dioxide yields (83 to 84 per cent) with dilution. In carbon tetrachloride, alkyl radicals are degraded rapidly by abstraction of chlorine from the solvent since no products derived from reactions of 4-phenylbutyl radicals with trichloromethyl can be found. Substantial amounts of hexachloroethane are produced. However, products from the reactions of 4-phenylbutyl radicals with each other and with acyloxy radicals are found. The authors attribute these products to diffusion-controlled destruction of secondary dissociation products.

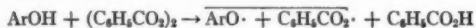


The really striking problem is the apparent fact that decarboxylation of two acyloxy radicals is faster than diffusion. It is remarkable that some phosgene, probably derived from the reaction of trichloromethyl with acyloxy, is produced. In benzene, alkyl radicals are apparently longer lived since they undergo extensive cyclization to form tetralin.

Smid, Rembaum & Szwarc (159) have reached similar conclusions concerning cage effects in the decomposition of propionyl and *n*-butyryl peroxides. The two compounds have virtually the same activation energies and frequency factors as acetyl peroxide. The constancy of activation parameters in the decomposition of a number of acyl peroxides is the only real evidence that decarboxylation is not part of the primary process [Bartlett & Greene (160)]. The addition of benzoquinone reduced the yields of  $C_2$  hydrocarbons from propionyl peroxide but leaves unchanged the yield of *n*-butane which is believed to arise from diffusion-controlled union of ethyl

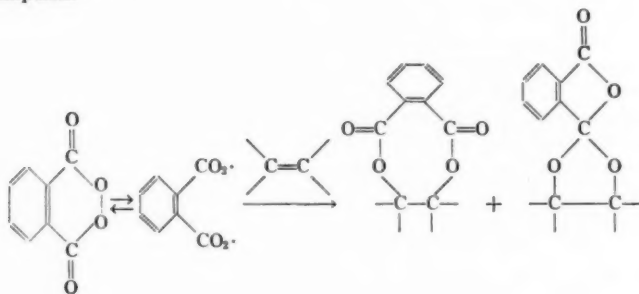
radicals. A small residual yield of  $C_2$  hydrocarbons at high scavenger concentrations comes from disproportionation of caged ethyl radicals. The residual  $C_2$  fraction contains more ethylene than ethane so some of the former must arise from an acetic acid-forming reaction. It is not all clear why the authors prefer cyclic decompositions of the peroxide as routes to ester, acid, and alkene. Granted that a cage effect controls alkyl radicals, it is difficult to see how one can avoid postulating cage reactions between alkyl and the acyloxy radicals formed in primary process.

Batten & Mulcahy (161) studied the reaction of phenol with benzoyl peroxide and find the kinetics to approximate second order. The rate is slower in dioxan than in benzene. At low concentrations, it is possible to observe the ordinary unimolecular peroxide decomposition and this process is mildly inhibited by phenol so that the decomposition rate passes through a minimum as the phenol concentration is reduced to zero. Batten (162) finds that the inhibitory efficiency of phenols at low concentration parallels their reactivity in the bimolecular reaction. A radical mechanism is suggested for the bimolecular reaction.



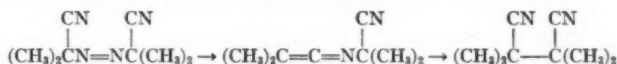
The reaction is supposed to be completed by a cage recombination although this does not seem to be necessary since phenols must be excellent scavengers for benzoyloxy radicals. Separated radicals might give the same products as those expected from primary recombination. The mechanism is, of course, kinetically indistinguishable from various polar and single-electron transfer mechanisms.

Greene (163) has found that monomeric phthaloyl peroxide has some very interesting properties. The rate of decomposition is unusually solvent dependent and is subject to acid catalysis. Decomposition in styrene is rapid but no polymerization results. In carbon tetrachloride, the peroxide reacts in stereospecific, bimolecular reactions with both *cis*- and *trans*-stilbene. Two products, both produced by *cis*-addition, are formed in each instance. All of the information is compatible with the view that the peroxide is rapidly equilibrated with a triplet state but does not compel this assumption.



The photochemical decomposition of cumyl peroxide and cumyl hydroperoxide [Norrish & Searby (164)] has turned out to be unusually interesting. The diperoxide is converted nearly quantitatively to cumyl alcohol in hexane but in carbon tetrachloride extensive fragmentation of cumyloxy radicals to ketones occurs. With 3130 Å, the main cleavage product is acetophenone but with 2537 Å acetone, the product of phenyl cleavage, predominates. The hydroperoxide gives acetone and phenol in carbon tetrachloride and small amounts of these products are also formed in hexane solution. The contrast between the fate of cumyloxy from the diperoxide and the hydroperoxide is attributed to an efficient cage reaction between cumyloxy and hydroxy-radicals.

*Decomposition of azo compounds.*—Questions of detail in the decomposition of azobisisobutyronitrile (AIBN) continue to attract interest. Roy *et al.* (165) have found that the quantum yield of organic iodide increases monotonically with iodine concentration when AIBN is photolyzed in toluene solutions containing iodine. The investigation was carried into the tenths molar concentration range without obtaining a saturation effect. Saturation at much lower concentration levels had been expected in the light of an earlier study [Hammond, Sen & Boozer (166)] of the thermal decomposition of AIBN. The importance of the observations derives from the assignment of an inefficiency in the production of scavengeable radicals in the thermal decomposition to primary recombination of radicals at a rate which is competitive with their diffusion rates. On the basis of the difference between photochemical and thermal decompositions, the authors conclude that the thermal decomposition must involve two paths, one radical and the other nonradical. They suggest that the path through the ketenimine intermediate detected by Talât-Erben & Bywater (167) does not involve radicals.



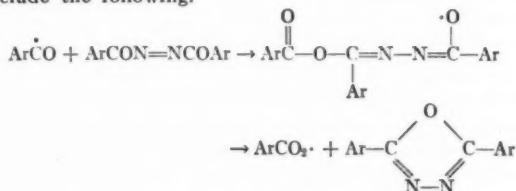
This explanation is not satisfying since it requires that the iodine effect in the photolysis must be due to the scavenging of geminate radical pairs  $2\text{R}\cdot + \text{I}_2 \rightarrow 2\text{RI}$ . Such an effect is imminently reasonable but requires that the thermal decomposition of AIBN to radicals must be uncomplicated by diffusion-recombination. The combination of requirements seems to be answered only by the assumption that  $\text{RN}_2\cdot$  is a primary product of thermal decomposition,—a possible but unattractive conclusion. Furthermore, unpublished observations in one of the reviewer's (G.S.H.) laboratory show unequivocally that the decomposition of the ketenimine intermediate produces radicals capable of initiating styrene polymerization.

Russell (168) has studied the rate of AIBN-initiated oxidations as a function of time. Plots of log rate vs. time at low conversions are linear, indicating that there is no oxygen effect on the rate of decomposition of the initiator.

Bevington (169) finds that the addition of  $\alpha,\alpha$ -diphenyl- $\beta$ -picrylhydrazyl to solutions in which AIBN is decomposing reduces the yield of tetramethyl-

succinonitrile but does not completely inhibit the formation of the dinitrile. The results of experiments in which conversions were low provide incontrovertible evidence that some dinitrile is produced from nonscavengeable precursors other than ketenimine.

Leffler & Bond (170) have studied the effects of both solvent and polar substituent variations on the rates of decomposition of diaryldiimides. Polar effects are substantial but the authors maintain that the decomposition does not change mechanism but represents an example of a homolysis by way of a strongly dipolar transition state. Amine-catalyzed and other fast decompositions of benzoyl peroxide are cited as other possible examples of the same phenomenon. Leffler's ideas on this subject are interesting and important and may well apply as indicated to the present problem, but the data certainly leave ample room for skepticism. The decomposition kinetics are untidy, and the reaction products are a partially resolved welter of chemical debris—natural phenomena for which Leffler & Bond can hardly be held responsible. Interesting steps which may account for some of the products include the following.



Overberger & Finestone (171) have made a careful study of the products from the decomposition of 1-azo-1,3-diphenylpentane at 90° and 144°. At the lower temperature, the decomposition is somewhat complicated by concomitant isomerization to a hydrazone but the conclusion is inescapable that 1,3-diphenylpentyl radicals give coupling in preference to disproportionation by at least a 9:1 ratio at both temperatures. The importance of the study derives from the use of the radical as a model for the growing chains in styrene polymerization.

DeTar & Relyea (172) produced 2-[*p*-toluyl]-phenyl radicals in the presence of carbon tetrachloride, bromotrichloromethane, bromodichloromethane, methylene iodide, and methyl iodide by treating diazonium salts from 2-amino-4'-methylbenzophenone with alkali. The radicals underwent three reactions; halogen abstraction from solvent, intramolecular hydrogen transfer to give the 2-benzoyl-5-methylphenyl radical followed by halogen abstraction, and cyclization to give, ultimately, 3-methylfluorenone. The amount of unrearranged halide varied with the reactivity of the solvent demonstrating that the reactions of the radical center with the second ring are discrete steps.

Gaylord *et al.* (173, 174, 175) has proposed an unusual radical displacement reaction as a source of nondegradative chain transfer in the polymerization of allyl esters. In essence, the suggestion is based upon the high





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# MOLECULAR ELECTRONIC SPECTROSCOPY

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This review summarises the experimental and theoretical work in the field of molecular electronic spectroscopy published in 1955 and 1956.<sup>1</sup> The inclusion of the foregoing year seemed to be necessary because the preceding review on the same subject was dedicated to a restricted part of this field. On the other hand, it was not possible to consider equally all topics of molecular electronic spectroscopy in the present review. The interesting subjects of spin intercombination spectra in organic molecules as well as in transition metal complexes have been excluded, because they were considered very thoroughly in the last year's review by Kasha & McGlynn (1) and by Moffitt & Ballhausen (2). Moreover, only a selected part of the work on diatomic spectra has been considered, and even the treatment of polyatomic spectra is far from being complete. A valuable article covering the same subject has been published by Callomon (3). Similar articles on special topics will be mentioned in due place.

Attention should be drawn to Mulliken's "Report on the Nomenclature for the Spectra of Polyatomic Molecules" (4). This report contains a number of recommendations for the use of symbols and notations of symmetry species, etc. Much of the present confusion in the notation of electronic states might be avoided if these recommendations were followed in further publications. In several cases, the reviewer has replaced the authors' notations by those recommended by Mulliken.

## EXPERIMENTAL TECHNIQUE

Experimental techniques have been improved in several directions. A variety of light sources, with continuous emission for absorption spectroscopy in the vacuum ultraviolet region, has been made available by the recent work of Wilkinson & Tanaka (5, 6, 7). Discharges in xenon, krypton, argon, and neon cover the region down to 800 Å. They are excited either by a condensed discharge or by microwave power. For the emission spectroscopy of organic molecules in the vacuum range, a lamp of the Schüler type has been described by El Khalafawi & Johannin-Gilles (8). The experimental problems of the vacuum ultraviolet region have been reviewed very thoroughly by Inn (9) and by Romand & Vodar (9a). The application of flash technique to the spectroscopy of short-lived radicals has been reviewed by Norrish & Thrush (10). A xenon flash lamp of synthetic sapphire for the

<sup>1</sup> The survey of the literature pertaining to this review was concluded in December, 1956; however, the November issues of several journals were not available at that time. The reviewer is indebted to many colleagues for making available to him reprints and preprints of their publications.



vacuum ultraviolet down to 1450 Å has been described by Nelson & Ramsay (11).

The new Bausch & Lomb concave diffraction gratings, with a resolving power of about  $10^5$  in first order, are extremely valuable for high resolution work. With fore-prisms they can be efficiently used in higher orders even in the vacuum region. An absorption cell for the measurement of vapor spectra at pressures up to 6000 bars has been described by Robin & Vodar (12), and an arrangement for the spectroscopy of liquids at such high pressures by Hughes & Robertson (13). A new type of absorption cell for low temperatures has been described by Jones & Keir (14). Better wavelength standards in the vacuum ultraviolet have been made available by Wilkinson's (15) accurate measurements of a large number of atomic lines in the region between 1940 and 875 Å.

#### DIATOMIC SPECTRA

By a reconsideration of existing data, Mathieson & Rees (16) have proposed several new assignments for different electronic states of the  $I_2$  molecule. The weak absorption at 2700 Å is ascribed to an upper repulsive  $^3\Sigma_u^+(O_u^-)$  state dissociating into two unexcited ( $^2P_{3/2}$ ) I atoms. The upper state of the Pringsheim-Rosen and Kimura-Miyaniishi absorption band systems is considered to be an ionic  $^3\Sigma_u^-(O_u^+)$  state instead of  $^1\Sigma_u^+$  as hitherto accepted. In connection with these and other reassignments, a revised potential energy diagram for  $I_2$  has been given. The continuous ultraviolet absorption of  $F_2$ -vapor has been reinvestigated by Stenzenberg & Vogel (17).

Hopfield's emission bands of  $O_2$  which appear in the condensed discharge in the presence of He were investigated by Tanaka, Jursa & Le Blanc (18), who found additional bands in the region from 1940 to 2360 Å. The transition seems to be  $\Sigma-\Sigma$  and its lower state identical with that of an absorption transition observed by Tanaka & Takamine (19) in the vacuum region.

The Lyman-Birge-Hopfield absorption bands of  $N_2$  were reinvestigated by Tanaka (20), who has reported 14 bands in the region between 1114 and 1450 Å. At lower wavelengths, additional bands have been observed which are tentatively ascribed to the transition  $C^3\Pi \leftarrow X^1\Sigma_g^+$ . In emission, the fifth positive system of  $N_2$  between 2030 and 2850 Å has been investigated by Lofthus (21). The vibrational and rotational analyses indicate that both states differ from other known states of this molecule. The emission spectrum of  $N_2$  in the vacuum ultraviolet from 920 to 1700 Å has been investigated by Wilkinson & Houk (22) with high resolution. Vibrational and rotational analyses were made for the band systems  $b^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$  and  $a^1\Pi_g \rightarrow X^1\Sigma_g^+$ . The ground state data agree with those obtained from recent Raman measurements. Rotational and vibrational perturbations are present in both excited states and also a new predissociation limit in the  $b^1\Sigma_u^+$  state at 106,758  $\text{cm}^{-1}$  (13.233 eV). With possible dissociation products  $^4S + ^2P$  or  $^2D + ^2P$  this is compatible with each of the values 9.756 or 7.373 eV for the dissociation energy of  $N_2$ , concluded from other predissociation data.

Wilkinson (23) has also investigated with high dispersion some bands of the  $C^2\Sigma_u \rightarrow X^2\Sigma_g^+$  emission spectrum of  $N_2^+$  in the vacuum ultraviolet region. The rotational analysis confirms the assignment of this transition, and the constants obtained agree with those found in earlier work. An unusual intensity distribution and vibrational perturbations in some levels are consistent with the assumption of an excitation mechanism involving inverse predissociation.

The absorption spectrum of NO in the region of 1400 to 2000 Å has been studied by Herzberg, Lagerquist & Miescher (24) at low temperature. Rotational analyses have been made for the overlapping  $\delta$  and  $\beta$  bands in the long wavelength part of this region, and data are given for their upper states  $C^2\Pi$  and  $B^2\Pi$ . Several bands of both systems show strong vibrational perturbations, indicating an almost complete mixing of their upper states in the environment of the crossing point of the potential energy curves. In the emission of a hollow cathode discharge, the  $\beta'$  bands of NO between 1600 and 1850 Å were investigated and analysed by Miescher (25). Because of the fine structure data, the system is ascribed to a  $B^2\Delta_i \rightarrow X^2\Pi_r$  transition to the ground state. The same author (26) has analysed the emission spectrum of  $NO^+$  in the range of 1350 to 1650 Å resulting from a transition  $A^2\Pi \rightarrow X^1\Sigma^+$ . From rotational perturbations in the  $A^2\Pi$  state he was able to calculate the rotational constant of the perturbing  $^2\Sigma^-$  state. With different light sources, Tanaka, Jursa & LeBlanc (27) investigated the absorption spectrum of CO in the region of 1070 to 2500 Å. The very strong fourth positive bands, belonging to the transition  $A^1\Pi \leftarrow X^1\Sigma^+$  and beginning at 1544 Å, have been extended to 1140 Å ( $v' = 20$ ). Isotope bands of  $C^{13}O^{16}$  have also been found up to high vibration levels. An intensity anomaly formerly observed by Schmid & Gerö (28) is not due to predissociation but probably to perturbation. From an extrapolation of the  $A^1\Pi$  vibrational bands, a dissociation limit of  $11.2 \pm 0.2$  eV is obtained. There are many indications that this dissociation leads to unexcited atoms, which would confirm the value of 11.111 eV suggested by other recent work. The different weaker band systems resulting from intercombination transitions have been studied also and extended to higher vibrational quantum numbers. With higher dispersion, the absorption spectrum of CO has been investigated by Herzberg & Hugo (29) in the region of 1230 to 1800 Å. Their main interest was in the Hopfield—Birge bands belonging to the forbidden transition  $a'^2\Sigma^+ \leftarrow X^1\Sigma^+$ , and in another new band system hidden under the much stronger bands of the fourth positive group which is assigned to a transition  $e^2\Sigma^- \leftarrow X^1\Sigma^+$ . Improved vibrational and rotational constants have been obtained for both excited states.

From a discharge through xenon and hydrogen in the presence of silicon, Douglas (30) obtained spectra of SiH and Si<sub>2</sub>. That of the latter molecule has four bands between 3490 and 3700 Å and further bands between 3980 and 4500 Å. The two systems are assigned to transitions  $L^3\Pi_g \rightarrow D^3\Pi_u$  and  $H^2\Sigma_u^- \rightarrow X^2\Sigma_g^-$  in analogy to transitions of the C<sub>2</sub> molecule. Several new band systems of the molecules PO, P<sub>2</sub>, and PS and of the ions PS<sup>+</sup>, NS<sup>+</sup>, and PO<sup>+</sup>

have been discovered by Dressler (31) in the near and far ultraviolet regions. A predissociation limit in the system  $E \rightarrow X^2\Pi$  of PO gives, under reasonable assumptions, a dissociation energy of 5.4 eV. Three emission band systems of AlF in the ultraviolet region have been analysed by Dodsworth & Barrow (32). They arise from transitions  $^3\Sigma \rightarrow a^3\Pi$  to a common lower state. Rotational analyses in the systems  $A^1\Pi_{g+}, B^3\Pi_1 \rightarrow X^1\Sigma^+$  of InF have been made by Barrow, Glaser & Zeeman (33). In the hollow cathode discharge, new band systems of MnF and MnBr in the red have been found by Hayes & Nevin (34). The blue-green bands of the manganese halides have been analysed vibrationally and assignments are attempted.

In an investigation of the visible absorption spectrum of BF, Brodersen & Sircé (35) found a convergence limit at  $29,915 \text{ cm}^{-1}$  for dissociation into  $B(^2P_{1/2}) + F(^2P_{3/2})$ , corresponding to a  $D_0$  value of 2.384 eV for the ground state. Two emission band systems of BF in the vacuum ultraviolet have been found and analysed by Brodersen & Mayo (36).

A new ultraviolet emission spectrum in the glow discharge of water has been observed by Benoist (37) and by Schüller & Michel (38). Its lower state is the same as that of a visible spectrum reported earlier by Schüller & Woelcke (38b) which is identified by Barrow & Downie (38a) as  $B^2\Sigma^+ \rightarrow A^2\Sigma^+$  of OH.

With cyanogen in a hollow cathode discharge and helium as a carrier, Douglas & Routly (39) obtained some new bands of CN in the near ultraviolet region corresponding to the transitions  $D^3\Pi \rightarrow X^2\Sigma$ ,  $D^3\Pi \rightarrow A^2\Pi$ ,  $F^2\Delta \rightarrow A^2\Pi$  and  $H^2\Pi \rightarrow B^2\Sigma$ . By an extension of this investigation to the vacuum region, Carroll (40) found and analysed further new band systems  $E^2\Sigma \rightarrow X^2\Sigma$ ,  $E^2\Sigma \rightarrow A^2\Pi$  and  $J^2\Delta \rightarrow A^2\Pi$  in the region of 1650 to 2100 Å. A Birge-Sponer extrapolation of the  $J^2\Delta$  state leads to a dissociation limit of  $87,500 \text{ cm}^{-1}$  above the ground state. With the reasonable assumption of a dissociation into  $C(^3P) + N(^2D)$  this limit is compatible with a ground state dissociation energy of  $66,000 \text{ cm}^{-1}$  suggested in earlier work.

#### POLYATOMIC SPECTRA

*Simple polyatomic molecules and radicals.*—The near ultraviolet spectrum of formaldehyde has been investigated by several workers. It seems to be generally accepted that all bands result from one excited state, and that the weak  $\alpha$ -foreband at 3700 Å in the absorption spectrum results from a Boltzmann level of the ground state. Cohen & Reid (41) have investigated absorption and fluorescence spectra in the vapor as well as in solution and proposed a vibrational analysis. Brand (42), from an investigation of  $H_2CO$  and of  $D_2CO$ , has given a rotational analysis leading to the result of a non-planar upper state with the angles  $HCH = 120^\circ$  and  $HCO = 116.5^\circ$ . With high resolution, the emission spectrum has now been investigated by Robinson & Benedict (43, 44). Their results are not too far from those of Brand, but the deviations from planar structure seem to be fewer.

The absorption spectrum of thiophosgene has been reinvestigated by

Burnelle (45) in the visible and ultraviolet region. The upper states of all band systems observed are found to be plane. The near ultraviolet absorption spectrum of oxalylchloride vapor has been studied by Sidman (46) in the region of 3000 to 3850 Å. From the dependence on temperature, it is concluded that it belongs to a mixture of two rotational isomers. The absorption of the *cis* isomer is continuous, whereas that of the *trans* isomer allows a partial vibrational analysis.

The very weak absorption system of SO<sub>2</sub> in the region of 3400 to 4000 Å has been measured and its vibrational structure analysed by Russell, Landrum & Vezey (47). As rotational constants are not available, the geometry of the excited state was determined from band intensities with the aid of the Franck-Condon principle. This calculation, performed by Coffman *et al.* (48), leads to an OSO angle of 124° in the excited state, to be compared with 119.5° in the ground state. From available data, Coon & Ortiz (49) have given a vibrational analysis of the 3000 to 5000 Å absorption system of ClO<sub>2</sub>. From data on vibrational and electronic spectra of SO<sub>2</sub>, CF<sub>2</sub>, ClO<sub>2</sub>, ClO<sub>2</sub><sup>-</sup>, COCl<sub>2</sub>, and CSCI<sub>2</sub>, Duchesne (50) has derived, by a detailed normal coordinate treatment, geometrical and potential energy constants for the most important electronic states of these molecules.

The absorption spectra of CH<sub>4</sub> and NH<sub>3</sub> have been investigated by Sun & Weissler (51) in the far vacuum ultraviolet from 375 to 1300 Å. CH<sub>4</sub> shows absorption increasing to a maximum at 960 Å which corresponds to the first ionisation potential of methane at 12.9 eV. Integration over the whole range leads to an *f* value of 6. In about the same range, the spectrum of CH<sub>4</sub> has also been measured by Ditchburn (51a). Sun & Weissler's measurements on NH<sub>3</sub> show some band structure down to about 1200 Å, and from there continuous absorption with maxima at 1130 and 750 Å, which seem to be connected with different ionisation potentials. The total *f* value is close to 6 also in this case.

There is an increasing interest in the spectra of unstable polyatomic radicals. Some investigations have been made on emission spectra, obtained in a King furnace or in a Schüller discharge. However, flash absorption spectroscopy seems to be the most powerful method. A valuable report on recent results has been published by Norrish & Thrush (10). Another review article on electronic spectra of polyatomic free radicals has been written by Ramsay (51b).

The absorption spectra of HCO and of DCO, obtained by flash photolysis of acetaldehyde, have been investigated now with high resolution by Herzberg & Ramsay (52) in the region of 4500 to 7500 Å. Formyl is the first polyatomic radical for which complete vibrational and rotational analyses have been made. It is found bent in the lower state with an angle of about 119.5°, but linear in the upper state. The transition is <sup>2</sup>Σ<sup>+</sup> ← <sup>2</sup>A'' with the transition moment perpendicular to the molecular plane. Possibly, the lower state is not the ground state but a low lying metastable state of the molecule. With DCO a second band system is observed near 7500 Å.

In the flash photolysis of hydrogen azide, Thrush (53) has obtained a new complex spectrum around 2700 Å, which he assigns to the  $N_3$  radical. The so-called  $\alpha$ -bands of ammonia, in the region of 4000 to 8300 Å, which had been known for a very long time from electric discharges and which later have been obtained in flash photolysis experiments with ammonia and hydrazine, have now been analysed and definitely assigned to the  $NH_2$  radical by Ramsay (54, 55). In its ground state, this radical is bent with an angle of  $103^\circ$ , whereas it seems to be linear in the upper state. The transition moment is perpendicular to the molecular plane. Two other polyatomic band systems have been observed in the high frequency discharge through ammonia at comparatively high pressures by Schüler, Michel & Grün (56) in the range of 5200 to 8500 Å. Spectra of  $PH_2$  and  $PD_2$  have been obtained by Ramsay (57) in the region of 3800 to 5500 Å from flash photolysis of phosphine. In spite of many previous attempts, no spectra of  $CH_3$  radicals had been found in the visible or in the near ultraviolet range. Recently, Herzberg & Shoosmith (58) succeeded in obtaining spectra at shorter wavelengths. Using dimethylmercury in a flash discharge, they found one band near 2160 Å and four diffuse narrow band groups between 1510 and 1300 Å. The vacuum bands form Rydberg series with an ionisation potential of  $79,380\text{ cm}^{-1}$  (9.840 eV).

Using a King furnace charged with silicon, Kleman (59) has obtained a complex spectrum between 4350 and 5630 Å which contains most of the blue-green bands emitted by some N-type stars. The spectrum is tentatively ascribed to the  $SiC_2$  radical and a vibrational analysis proposed.

Recently, Gaydon (60) had assigned the characteristic visible flame spectra of alkaline earth salts to triatomic radicals like  $CaOH$  or  $SrOH$ . This assumption has been confirmed by the investigations of James & Sugden (61) and of Charton & Gaydon (61a), who found isotopic shifts in the spectra of arcs burning in light or in heavy water atmospheres. It seems, however, that other carriers also take part in these spectra.

*Olefinic and polyene molecules.*—Wilkinson & Mulliken (62) have investigated the vapor absorption spectra of  $C_2H_4$  and  $C_2D_4$  with high dispersion down to 1500 Å. The absorption consists of a continuum, beginning at about 2000 Å with a maximum at 1620 Å and corresponding to the transition  ${}^1B_{1u} \leftarrow {}^1A_{1g}(V \leftarrow N)$ . Superimposed on this continuum are a progression of broad weak bands which can be followed to 1750 Å and several pairs of much stronger Rydberg bands ( $R \leftarrow N$ ) at shorter wavelengths. A partial vibrational analysis has been made for all states. It is consistent with the assumption of a  $90^\circ$  twisted V state with an energy minimum at about  $40,000\text{ cm}^{-1}$ . Wilkinson (63) has extended this investigation to the range of 1300 to 1500 Å where further sharp Rydberg bands occur. The twisting frequencies of the different R states show isotopic shifts which are much larger than those expected for a simple cosine potential. With low resolution, new quantitative extinction measurements on ethylene have been made by Hammond & Price (64). They lead to an  $f$  value of 0.20 for the  $V \leftarrow N$  transition.

Further work on the spectra of alkyl substituted ethylenes has been done

with lower resolution. Stokes & Pickett (65), in continuation of their former work on vapor absorption spectra, have now investigated the bridged ring compound bicyclo (2,2,1)-2-heptene. Potts (66) has measured the quantitative absorption spectra of trimethylethylene, tetramethylethylene, hexene-1 and cyclohexene at 80°K. in rigid solution. It is found that with decreasing temperature the long wavelength shoulder of the strong  $V \leftarrow N$  transition is diminished considerably. This unusual behavior is explained by the non-planar equilibrium configuration of the  $V$  state corresponding to a negative slope of the potential energy curve. A deviation from the planar configuration of the ground state by thermal motion (or by crowded substituents) must lead, therefore, to increasing absorption at higher wavelengths. When the shoulder of the strong  $V \leftarrow N$  transition is removed at low temperature, a much weaker band system appears in the region of 2100 to 2500 Å which presumably corresponds to the intercombination transition  ${}^3B_u \leftarrow {}^1A_g(T \leftarrow N)$ . The spectra of several cyclic olefinic compounds at room temperature have been measured by Wheeler (67). In molecules with ring strain they show considerable bathochromic shifts. Quantitative absorption spectra of the vapors and solutions of more than 40 olefinic and diolefinic hydrocarbons in the range between 1700 and 2300 Å have been measured with medium resolution by Jones & Taylor (68).

The investigation of higher members of the polymethine series is still of considerable interest. It has been known for a long time that, at least for the first members of this series, the square of the wavelength  $\lambda_{\max}$  of the first absorption region increases linearly with the number  $n$  of conjugated double bonds. As there seems to be no acceptable theoretical foundation for this relationship, deviations should be expected, at least, for the higher members of the series. Previously, Naylor & Whiting (69) had found such deviations for dimethylpolyenes with  $n$  values between 6 and 12, indicating a tendency to approach a final  $\lambda_{\max}$  value for the infinite chain. However, Bohlmann & Mannhardt (70) who made special efforts to ensure the all-*trans* configurations of their dimethylpolyenes, found the relation valid up to  $n=10$ . The spectra of conjugated polyene aldehydes up to  $n=7$  have been measured by Krauss & Grund (71) together with those of their complexes with  $\text{BF}_3$ ,  $\text{FeCl}_3$  and  $\text{SbCl}_5$ . Polyacetylenes show similar regularities as the corresponding polyenes. Beer (72) has followed the absorption spectrum of dimethyltriacetylene vapor into the vacuum region. Furthermore he has measured the fluorescence and phosphorescence spectra of several substituted polyacetylenes in a rigid solvent at 100°K. Absorption spectra in solution of several phenyl substituted cumulenes have been measured by Bohlmann & Kieslich (73).

Previously, Schüler & Reinebeck (74) had obtained in the electrode discharge of acetylene, as well as of different aromatic hydrocarbons, a visible spectrum which they called "T" spectrum. This has now been investigated with high resolution by Callomon (75). From vibrational and rotational analyses, together with other evidence, it is concluded that the diacetylene posi-



tive ion  $C_6H_2^+$  is the carrier of the "T" spectrum. It is assigned to a transition  $A^2\Pi_u \rightarrow X^2\Pi_g$ .

*Aromatic hydrocarbons.*—The vacuum ultraviolet spectra of  $C_6H_6$  and  $C_6D_6$  have been photographed by Wilkinson in the region of 1300 to 1850 Å with high dispersion (76). From more than 100 bands, four Rydberg series were identified converging to an ionisation potential of  $74,587\text{ cm}^{-1}$  (9.247 eV) for  $C_6H_6$ . The vibrational analysis shows long progressions of a nontotally symmetric  $e_{2g}$  vibration. This is explained by the assumption of distorted nuclear equilibrium configurations in the Rydberg states with  $D_{2h}$  symmetry only which might result from Jahn-Teller effect in degenerate  $^1E_{1u}$  states of  $D_{6h}$  symmetry. Quantitative extinction measurements for benzene in the region between 1600 and 2000 Å have been made by Hammond & Price (64). The  $f$  values calculated are 0.094 and 0.88, respectively, for the first and second transition in this region which, by most authors, are assigned as  $^1B_{1u} \rightarrow ^1A_{1g}$  and  $^1E_{1u} \rightarrow ^1A_{1g}$ . This assignment of the first of these transitions in the range of 1850 to 2000 Å has now been questioned again by Dunn & Ingold (77). Their objections are based on a consideration of the—unfortunately very diffuse—vibrational structure of this transition in the vapor spectrum which does not show the Boltzmann bands to be expected for this assignment. As some structural details might be attributed to Jahn-Teller splitting, the authors prefer to assign the transition to an upper  $^1E_{2g}$  state. It should be mentioned, however, that this assignment makes it extremely difficult to understand the relations between the spectra of benzene and other aromatic compounds.

The very weak absorption bands of liquid benzene near 3300 Å which are the mirror image of the phosphorescence spectrum are ascribed to an intercombination transition with an upper  $^3B_{1u}$  state. As Evans (78) has found, these bands disappear in the absence of oxygen. Obviously, if that assignment is to be maintained, the intensity of the bands is determined essentially by the presence of paramagnetic molecules.

The vapor absorption spectrum of hexamethylbenzene has been followed down to 1300 Å by Nelson & Simpson (79). Under low resolution it shows the main absorption regions of the parent compound benzene shifted more or less to the red. In addition to these, an extra band system at 2350 Å ( $\epsilon_{\max} \sim 2400$ ) is observed in the vapor but not in solution.

The far ultraviolet absorption spectra of benzene, toluene, and *p*-xylene have been measured by Potts (80) at 90°K. in aliphatic hydrocarbon glasses. The 1850 and 2100 Å band systems show, under these conditions, enough structure to allow partial analyses. These support the assignment of these band systems to  $^1E_{1u}$  and  $^1B_{2u}$  upper states, respectively, of benzene.

The blue hydrocarbon azulene has quite unusual fluorescence properties. Beer & Longuet-Higgins (81) have observed that, under suitable excitation, it shows ultraviolet fluorescence. This fluorescence is most intensive at low temperature in a rigid solvent, but persists even at room temperature. It



corresponds to a transition from the second excited singlet state  $^1L_a$  down to the ground state, whereas usually excitation of higher excited states leads, via radiationless transitions, to fluorescence emission from the lowest excited state. This anomalous behavior of azulene seems to be related to the unusually large energy separation between these two states. Excitation of the lower state  $^1L_b$  does not give any detectable fluorescence. The same behavior has been reported by Visvanath & Kasha (82) also for some methyl substituted azulenes.

Wolf (83) has measured and partially analysed the absorption and fluorescence spectra of a number of methyl substituted naphthalenes at 90°K. in rigid solvent. The 0,0 bands of their first transitions are much stronger than those of their parent compound. The 0,0 frequencies of the first and second band system can be represented approximately by vector rules similar to those valid for substituted benzenes, whereas the position of the third system near 2200 Å depends solely on the number of substituents. The absorption spectra of naphthalene, 2-methylnaphthalene and 2,6-dimethylnaphthalene have been investigated also by McConnell & Tunnicliffe (84). The increasing intensity of the 0,0 band of the first transition shows that its low intensity in naphthalene does not result from symmetry forbiddenness and is in favor of the usual assignment  $^1B_{2u} \leftarrow ^1A_{1g}$  in Mulliken's notation (4).

The absorption spectra of 1,2-benzanthracene and all of its 12 mono-methyl-derivatives have been measured in rigid solution at 170°K. by Sandorfy & Jones (85). Most of the transitions observed can be assigned to three different progressions, corresponding to  $^1L_b$ ,  $^1L_a$ , and  $^1B_b$  in Platt's nomenclature. The spectra of aromatic hydrocarbons in the crystalline state are reviewed in a later section of this article.

Absorption and emission spectra of short living radicals, derived from aromatic hydrocarbons, have been obtained in different ways. Porter & Wright (86), in flash photolysis experiments with the vapors of toluene, ethylbenzene, benzylchloride, and similar compounds, obtained the same sharp absorption spectrum. This spectrum, with its main band at 32,760  $\text{cm}^{-1}$ , is assigned to the benzyl radical. A similar spectrum, with the usual red shift, has been obtained by Norman & Porter (87) by irradiation of the above mentioned compounds in rigid solvents at 77°K. In the same way, the absorption spectra of several other hydrocarbon radicals have been obtained under moderate irradiation at low temperature, where those radicals are fairly stable.

The benzyl radical seems also to be the carrier of a visible emission spectrum, which has been observed some years ago by Schüler and co-workers (88) in the glow discharge of different benzene derivatives. This spectrum extends from 22,330  $\text{cm}^{-1}$  to the red, and must, therefore, belong to another transition than the absorption spectrum observed by Porter's group. An explanation for it has been given by Schüler & Michel (89) and by Bingel (90).

The vapor absorption spectrum of cyclopentadienyl has been obtained by Thrush (91) from the flash photolysis of cyclopentadiene.

*Other aromatic compounds.*—A large number of substituted aromatic hydrocarbons have been investigated in the vapor state as well as in solution. The near ultraviolet absorption spectra have been measured and partially analysed in the vapor state by Anno & Matubara (92) and by Asundi & Joshi (93). Among the three phenylenediamines which have been investigated by Sado & Anno (94), only the *meta* isomer shows enough structure for a partial analysis. The vapor absorption of 1,2,4,5-tetrachlorobenzene has been investigated and analysed by Matubara & Anno (95). Solution spectra of a large number of trisubstituted benzenes have been reported by Doub & Vandenbelt (96) as well as by Forbes & Mueller (97). These spectra show obvious regularities as far as steric hindrance is absent. Some new absorption data on *p*-substituted acetophenones have been given by Tanaka, Nagakura & Kobayashi (98). Braude & Sondheimer (99) have measured solution spectra of different substituted benzaldehydes, acetophenones, and related compounds. Kiss & Muth (100) have investigated the spectra of some aromatic sulfides and selenides with internal —S—, —S—S— etc., bridges. As Weller (100a) has found, the fluorescence of salicylic acid in alcoholic solution is emitted by a *zwitterion*, formed by proton transfer from the hydroxy group to the carbonyl group in the excited state.

The absorption maxima of all monofluoro- and mononitro-derivatives of phenanthrene and of triphenylene have been reported by Bavin & Dewar (101). Solution spectra of the completely chlorinated aromatic hydrocarbons octachloronaphthalene and decachloropyrene have been measured by Mosby (102). The extremely broad band structure of these spectra is ascribed to a nonplanar molecular configuration. Aromatic amines give salts with alkali metals in suitable nonaqueous solvents. The absorption spectra of such salts derived from 2-naphthylamine and 2-aminoanthracene have been investigated by Förster & Renner (103).

The absorption spectra of different diazanaphthalenes and of some of their derivatives have been investigated by Hirt, King & Cavagnol (104) with special interest in their  $\pi$ - $n$  bands at the red side of the stronger  $\pi$ - $\pi$  bands. Some hydroxy- and amino-substituted acridines and phenacines have been studied in their different ionisation stages by Perkampus (105) and by Bartels (106). Thomas & Martell (107) have investigated the influence of substituents on the spectra of tetraphenylporphines. The spectrum of chlorin, the parent compound of chlorophyll, has been measured by Eisner & Linstead (108) and that of bacteriochlorophyll by Barnard (109). A large number of merocyanines have been investigated by Lauerer *et al.* (110) in different ionisation stages at room temperature and below.

*Interaction effects in solution.*—Solution spectra depend to a certain degree on the interaction between solute and solvent molecules. Pronounced interaction effects may occur in the presence of other compounds feasible to

complex formation as well as in more concentrated solutions. These effects may consist in displacements or intensity changes of bands already present or even in the appearance of additional absorption regions. Very often these effects are different and more pronounced in the fluorescence spectra.

Robertson & Matsen (111) investigating the 2600 Å absorption region of benzene in hexane up to pressures of 6000 bars found considerable red shifts and broadening of the individual bands due to dispersion forces. Ferguson (112) has compared the 0,0 bands of many substituted benzenes in vapor and hydrocarbon solutions. The red shifts do not depend on the intensities of the corresponding transitions as it might be expected from an earlier theory.

Larger effects occur in the spectra of polar compounds dissolved in polar solvents. They are especially large in the fluorescence spectra, because the time interval between absorption and emission process allows orientation of solvent dipoles to take place. Mataga, Kaifu & Koizumi (113) have investigated and discussed such shifts in the fluorescence spectra of substituted naphthalenes in polar solvents. From similar investigations, Lippert (114) has estimated the dipole moments and solute-solvent interaction energies in the excited states of the molecules of several meropolar compounds such as 4-dimethylamino-4'-nitrostilbene. Similar solvent effects in the spectra of meropolar dyes have been investigated by Hünig, Rosenthal & Raquardt (115, 116). A general theory of solvent effects on absorption and fluorescence spectra under inclusion of dispersion and dipole interaction forces has been presented by McRae (117).

In other cases, solvent interactions are of a more specific nature and may be interpreted in chemical rather than in physical terms. In an investigation of the absorption spectra of pyridazine, Brealey & Kasha (118) have found that the individual bands of the weak  $\pi \rightarrow \pi^*$  transition retain their positions in different hexane-alcohol mixtures. The apparent blue shift in this transition results only from intensity changes of these bands and must be due, therefore, to the formation of well defined hydrogen-bonded complexes. Mataga, Kaifu & Koizumi (119) have investigated the shifts of the absorption and fluorescence spectra of  $\beta$ -naphthol in mixtures of hexane with methylacetate and similar compounds. From the differences observed in both kinds of spectra, they conclude that a much stronger hydrogen bonding occurs in the excited state of the molecule. The ionization processes of aromatic hydroxy compounds in their excited states, formerly inferred from fluorescence spectra, have now been established by Breitschwerdt, Förster & Weller (120) also from absorption spectra under flash irradiation.

Spectroscopic work on molecular complexes of the donor-acceptor type has been done by many workers. In typical cases, these complexes show an additional absorption region, resulting from an intramolecular electron transfer transition. Briegleb, who did much of the earlier work in this field, & Czekalla (121) have published new absorption data on *s*-nitrobenzene complexes with various other aromatic compounds. According to Czekalla (122),

in some of these complexes the electron transfer transition takes place also in emission at low temperature. Complexes of *s*-trinitrobenzene with pyridine-N-oxides have been studied by Ross, Kelley & Leber (123) and those of *p*-benzoquinone with various aromatic compounds by Kuboyama & Nagakura (124). Some new work on complexes of halogen molecules with olefinic and aromatic compounds has been published by Murakami (125, 126), and the usefulness of these spectra for analytical purposes has been discussed by Long & Neuzil (127). Complex formation of aromatic and olefinic hydrocarbons with aluminum halides and similar reagents has been studied by Luther & Pockels (128) and by Fairbrother & Field (129).

In several cases, it might be doubtful whether the presence of a charge transfer band indicates the formation of a stable complex at all. Evans (130) has found such bands in the spectra of bromine and iodine even in paraffin hydrocarbon solvents, where Kortüm & Vogel (131), from solubility measurements, did not find any indication of complex formation. The increasing absorption of hexane and cyclohexane below 2300 Å in the presence of oxygen, reported by Munck & Scott (132), might be a similar case. According to Mulliken (133), even the short contact during a collision of donor and acceptor molecules might be sufficient to produce an electron transfer transition.

Interaction between like molecules leads to deviations from Beer's law in the absorption spectra of iodine in *n*-heptane and carbontetrachloride between 2500 and 3500 Å. From these deviations, De Maine (134) has concluded the existence of dimer complexes. With ionic dyes in aqueous solution, such deviations are of common occurrence. In the case of the univalent cation of Neutral Red, they have been studied extensively by Bartels (135) who has interpreted them by the formation of dimers and tetramers. Fluorescein, eosin and rhodamine-B have been investigated by Förster & König (136). Only dimers are formed even in the most concentrated solutions of these dyes. Their spectra show double maxima which are interpreted by resonance splitting of the excited states. The well-known sharp long wavelength band of pseudoisocyanine which formerly was observed in concentrated aqueous solution has been reported by Zimmermann & Scheibe (137) to occur also in alcoholic solution at 90°K. From the dependence on concentration, it is concluded that, contrary to other cases, the band belongs to an associate of a few molecules only. With a related compound, Käufer & Scheibe (138) have observed a similar association band also in films spread on a water surface.

With different merocyanine dyes solvent and concentration effects have been studied by Hirschberg, Knott & Fischer (139) in water-alcohol mixtures. Additional long wavelength bands in the spectra of *N*-ethyl-phenacyl and Wurster's blue have been found by Hausser (140) in a rigid solvent at 90°K. and tentatively attributed to dimer formation. In a comparison of the absorption spectra of indigo dyes in solution and the solid phase Weinstein & Wyman (141) have found large bathochromic shifts which are absent in

derivatives with bulky substituents and are, therefore, explained by association. The dependence on concentration of the triplet-triplet absorption spectra of acridineorange has been studied by Zanker (142). A strong component at higher wavelengths in the fluorescence spectrum of pyrene solutions appearing at higher concentration has been observed by Förster & Kasper (143). In the absence of any changes in the absorption spectrum, dimer formation in the excited state by a collisional process is supposed. Berg & Nordén (144) have observed a similar effect, but less pronounced, in the fluorescence spectrum of 3,4-benzopyrene.

Very weak interaction only which cannot be detected by other spectral effects is necessary to produce sensitized fluorescence by intermolecular transfer of excitation energy. A very striking example for this has been given by Bowen & Brocklehurst (145) with 9-chloroanthracene and pyrene in rigid solution where trivial reabsorption or collisional processes are ruled out definitely. The mean transfer distance was found to be 34 Å in this case. Similar investigations with anthracene and tetracene have been made by Ferguson (146) and with toluene and *p*-terphenyl by Cohen & Weinreb (147). Energy transfer between like molecules has been further studied by Galanin (148) who investigated the fluorescence of solutions of fluorescein, rhodamine, and acridineorange. Sensitization of phosphorescence by energy transfer between triplet states has been observed by Terenin & Ermolaev (149) between benzophenone and naphthalene as well as in other systems in rigid solution.

*Polarized spectra.*—In molecular crystals the absorption spectrum changes with the direction of the electric vector of the lightwave. If one knows the molecular orientation towards the crystallographic axes, it should be possible to derive, therefrom, the directions of the vibronic and electronic transitions within the molecule. Similar conclusions should be possible from polarized fluorescence spectra. In a pure crystal, however, with more than one molecule in the unit cell, complications arise from the strong interactions between close lying molecules of different orientations. These may be avoided by using mixed crystals, where the compound to be investigated is embedded with well defined molecular orientation in a host crystal which absorbs at shorter wavelengths. Unfortunately, it is very difficult to derive, in an independent way, the orientation of the foreign molecules towards the host crystal axes. But in suitable cases, this may be assumed with a high degree of certainty from geometrical considerations.

McClure (150) has completed his former investigations on naphthalene in durene single crystals by measuring with high resolution at 20°K. the absorption and fluorescence spectra of the deuterated compound. The absorption spectrum of the first transition is quite different in both polarization components. Under the assumptions made concerning the orientation between naphthalene and durene molecules, the intensity ratios are consistent with long axis polarization of the electronic transition or, in other words, with an  $^1B_{2u}$  upper state (Mulliken's nomenclature). This agrees with

Platt's classification of this state as  $L_b$  and with the result of all recent theoretical work. As, however, experimentally as well as theoretically the transition moment is ("accidentally") very low, the symmetry assignment predicted might be regarded as more or less formal. Naphthalene in durene has been investigated also without polarization analysis by Wolf (151) who disagrees with the orientation supposed by McClure.

Azulene has been investigated by Sidman & McClure (152) in naphthalene solid solution at 20°K. The visible absorption region is found to be polarized perpendicularly to the (long) molecular axis, corresponding to a  $^1B_2$  ( $L_b$ ) upper state. The first ultraviolet transition shows longitudinal polarization as expected for an  $^1A_1$  ( $L_a$ ) upper state.

A preliminary investigation of the polarized absorption spectrum of anthracene in naphthalene has been made by Maier & Wimmel (153). Spectra with higher resolution have been obtained at 20°K. from anthracene in naphthalene and in phenanthrene by Sidman (154). Both investigations show the first transition of the anthracene molecule to be short axis polarized ( $^1B_{1u}$  or  $L_a$  upper state), in agreement with theoretical work. The same is true for tetracene investigated by Sidman (155) in naphthalene as well as in anthracene. The same author (156) has also studied the pericondensed hydrocarbon acepleiadiene (an odd ring isomer of pyrene) together with its hydrogenation product acepleiadiene, both in pyrene solid solution. In most of this work with mixed crystals at low temperature, the fluorescence spectra were also investigated and found to be nearly unpolarized. With anthracene in phenanthrene this phenomenon has been studied by Sidman (154) at different temperatures. The fluorescence is nearly unpolarized at 20 and 77°K. but definitely polarized at 300°K. with more intensity along the short molecular axis in agreement with the absorption spectrum. The reasons for this depolarization of fluorescence at low temperature are not completely understood.

Another method to obtain oriented solutions of aromatic molecules has been applied by Albrecht & Simpson (157). By irradiation with polarized light of rigid solutions of tetramethyl-*p*-phenylenediamine, they obtained partially oriented solutions of this compound as well as of its photo product Wurster's Blue. The direction of the visible transition of the latter compound was found by inspection of the crystal. Therefrom, the directions of all transitions in both molecules were determined by polarized absorption measurements on the irradiated solution.

Oriented molecules are also present in liquid crystals. Maier & Saupe (158) have used this for a study of the directional absorption properties of 4,4'-dimethoxy-azoxybenzene. The first absorption region near 3500 Å of this compound is almost completely polarized along the liquid's optical axis which most certainly corresponds to the longest molecular diameter. Intermolecular interaction effects which might be expected here, as well as in other pure crystals, do not seem to be important in this case.



Polarized absorption and fluorescence spectra of pure single crystals may be used as well to investigate the intramolecular directions of electronic transitions. But the results must be analysed very carefully for reasons considered above. Hexamethylbenzene is especially suitable for such an investigation because its crystal contains only one molecule per unit cell. It has now been studied down to 1720 Å with low resolution by Nelson & Simpson (159). In the whole range the absorption is polarized predominantly in the molecular plane. High dispersion work on the same compound has been done by McClure & Schnepf (160) at 20°K. in the near ultraviolet region. Whereas the main part of the first absorption region is polarized in the molecular plane, the weak 0,0 band is definitely polarized perpendicularly indicating a lower symmetry than  $D_{6h}$  for the molecule in its crystalline environment. *p*-Dimethoxybenzene which has been investigated with medium dispersion by Albrecht & Simpson (161) shows predominant short axis polarization in the 2900 Å region and long axis polarization in the next one.

The absorption spectrum of crystalline naphthalene has been investigated at 20°K. with high resolution by McClure & Schnepf (162) and with medium resolution but quantitatively at 90°K. by Wolf (163, 164). These authors agree that the polarization of the first transition including its 0,0 band indicates a transition moment along the short molecular axis. This is considered by Wolf to be true also for the free molecule. McClure & Schnepf, however, who assume the first excited state of the free molecule to be  ${}^1B_{2u}$  with longitudinal transition moment, explain the inversion of the polarization ratio in the crystal by induced mixing with the high transition moment of the close lying  ${}^1B_{1u}$  state. A Davidov splitting of 166  $\text{cm}^{-1}$  exists in the 0,0 band but not in the vibronic levels of the first transition. A calculation by Craig & Walsh (165) of polarization ratios and splitting values in the second system of naphthalene supports the assignment of this and of the third system to  ${}^1B_{1u}$  and to  ${}^1B_{2u}$ , respectively.

Fewer difficulties have been encountered in an investigation of the phenanthrene crystal by McClure (167). There is a small Davidov splitting of 43  $\text{cm}^{-1}$  between the 0,0 bands of the first transition. Its polarization ratio indicates a transition moment along the (short) molecular axis corresponding to an  ${}^1A_1$  ( $L_b$ ) upper state.

The work of Craig & Hobbins (168, 169) on the spectra of anthracene crystals has now been published in detail and extended by Bree & Lyons (170). Two absorption regions, one at 2700 Å and another one with different polarization at about 2000 Å, are interpreted as Davidov components of the 2500 Å solution transition which, therefrom, is found to be  ${}^1B_{2u} \leftarrow {}^1A_{1g}$ . This extremely large splitting is attributed to the high transition moment together with an orientation which favors strong dipole interaction. The weaker absorption system at 3800 Å has been investigated at low temperature with high resolution. All bands occur in both polarization components and have only a very small Davidov splitting, even in the 0,0 band. The polarization



ratios observed and the small splitting are consistent with short axis polarization and a  ${}^1B_{1u}$  ( $L_a$ ) upper state if crystal induced mixing with the strong second  ${}^1B_{2u}$  state is taken into account. This interpretation has been discussed further by Lyons (171), Fox & Yatsiv (172) and by Craig & Walsh (173). With high resolution the first absorption system and the fluorescence spectrum of anthracene have been investigated further at 4°K. by Sidman (166). The appearance of weak forebands in the absorption spectrum and a considerable gap between its 0,0 band and the fluorescence origin are taken as evidence for a trapped exciton state in the crystal. New measurements of the polarization of anthracene fluorescence have been made by Ferguson & Schneider (174).

Further investigations on polarized absorption spectra have been made by Sidman (175, 176, 177) with crystals of sodium nitrite, biacetyl, benzoquinone, and other quinones, and by Yamada & Tsuchida (178) on tropolone- $\text{Cu}^{++}$ -complexes.

#### THEORETICAL ASPECTS

The quantum mechanical methods for the calculation of electronic energies and transition moments have been further developed and applied to a large number of molecules. Unfortunately, the restricted space allows limited consideration of only some of the work done in this field. Most of it has been done on  $\pi$ -electron spectra of unsaturated and aromatic molecules along the lines of MO (Molecular Orbital) theory using either Hückel's LCAO (Linear Combinations of Atomic Orbitals) description or the FE (Free Electron) variant. Whereas the naive application of these methods under neglect of specific electronic interaction is usually sufficient for ground state properties, it is unreliable for excited states. In more refined calculations antisymmetrical product wave functions of different orbital configurations must be considered and electronic interaction taken into account explicitly. Such a procedure is extremely difficult for more complicated molecules and, nevertheless, still insufficient in purely theoretical calculations. This may be seen, for instance, from Nesbet's treatment of butadiene (179). The method seems to be reliable, however, as a semiempirical one with a reasonable adjustment of a few parameters. This still holds even if the method is simplified by the neglect of differential overlap between atomic orbitals which has been introduced by Pariser & Parr (180, 181) in their earlier calculations on ethylene, benzene, and simple heterocyclic molecules. The same method has now been applied by Pariser (182) in a calculation of energy levels and transition moments in the series of polyacenes up to pentacene. With three parameters adjusted so as to fit the benzene spectrum and with the inclusion of many orbital configurations, very reasonable results are obtained. Similar calculations on aromatic hydrocarbons with better (self consistent) orbitals, but with less configuration interaction, have been made by Pople (183).

Other calculations based on the same principles have been made by Schiess & Pullman (184) on cyclooctatetraene, by Julg & Pullman (185) on fulvene and heptafulvene, by Serre (186) on different vinylacetylenes and cumulenes, and by Murrell & Longuet-Higgins (187) on the cycloheptatriene cation. The naphthalene molecule has been treated by Moser & Lefebvre (188) with different refined LCAO methods.

A general LCAO treatment of odd alternant hydrocarbon radicals and ions under inclusion of configuration interaction has been given by Longuet-Higgins & Pople (189). As Longuet-Higgins, Murrell & McEwen (190, 191) have shown butadiene, styrene, cyclooctatetraene, and similar molecules may be reasonably considered as composite systems and their excited states treated either as locally excited or as electron transfer states between their components. A simplified treatment by Nagakura & Tanaka (192, 193) of certain transitions in substituted benzenes as arising from "intramolecular charge transfer" uses the same point of view. Inductive substitution effects in alternant hydrocarbons have been treated by Murrell & Longuet-Higgins (194) and mesomeric effects by Murrell (195). A general theory of both kinds of substitution effects has been given by Goodman, Ross & Shull (196).

Electronic interaction has also been incorporated into the FE variant of MO theory. Kuhn (197) and Labhart (198) have reported some results obtained by different methods. Extensive semiempirical calculations have been made by Ham & Rüdénberg (199) on a large number of aromatic hydrocarbons leading to similar results as those of Pariser's LCAO treatment.

The valence bond method has been neglected during the last years. It has now been applied by Simpson (200) in a discussion of the spectra of different unsaturated and aromatic molecules. Features of both methods have been used by Platt (201) in a comprehensive treatment of cyanine dyes and polyenes.

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# VIBRATION-ROTATION SPECTROSCOPY<sup>1</sup>

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The vigor and wide interest displayed in the field of molecular spectroscopy has continued without abatement during 1956. This review must, therefore, omit many papers of more than passing interest in order to indicate some of the significance of current research. The character of this work and the development of trends are illustrated with selections from the current literature and it is inevitable that these are influenced to some extent by the personal interests of the reviewer. The latest, comprehensive reviews of infrared spectroscopy by Gore (1) and of Raman spectroscopy by Stamm (2) list specific problems to which these techniques have been recently applied.

## VIBRATION SPECTRA

The first step in the analysis of the vibration-rotation spectrum of a polyatomic molecule is the assignment of frequencies to the fundamental modes of vibration. This may be followed by the determination of the absolute intensity of the bands and an analysis of the rotational fine structure when the moments of inertia of the molecule are sufficiently small so that the detailed band structure may be resolved. These data may then be applied to obtain information about the structure of the molecule, the nature of the chemical bonds, and the forces acting between the several atoms.

The assignment of frequencies, of necessity, proceeds from the simpler to the more complicated molecules. Its *modus operandi* involves the use of symmetry (selection rules) and comparison with similar molecules, including those with isotopic atoms. Initial treatments of a molecule frequently involve tentative assignments and are often incomplete. Better data resulting from improving instrumentation and the accumulation of information on similar molecules eventually lead to a complete and reliable assignment. As indicated in Table I, a large number of simple molecules have been studied in the past year and frequency assignments made. The heavy concentration of effort on the halogen derivatives of methane, ethane, and ethylene, so evident for the last several years, is definitely slackening. More complicated organic molecules are being treated and a healthy interest is being displayed in molecules containing atoms from all parts of the periodic table. Unsolved problems of bonding in inorganic molecules are being studied.

Among the organic molecules, attention should be called to the careful infrared study of  $C_6D_6$  by Miller (44). This work seems to have established all the fundamentals of this molecule and confirmed the assignments of Mair

<sup>1</sup> The survey of literature pertaining to this review was concluded in December, 1956.

TABLE I

VIBRATIONAL SPECTRA OF SMALLER MOLECULES OR IONS

Molecule	Spectra*	Reference	Molecule	Spectra*	Reference
LiH	I	(3)	UF <sub>6</sub>	R	(30)
TCN	I	(174)	KAg(CN) <sub>3</sub>	I	(33)
CICN	I	(4)	Cu(CN) <sub>3</sub> <sup>-</sup>	I	(34)
BrCN	I	(4)	Pt(CN) <sub>4</sub> <sup>-</sup>	IN	(35)
ICN	I	(4)	Ni(CO) <sub>4</sub>	I	(36)
SiO <sub>2</sub>	I	(5)	Cr(CO) <sub>6</sub>	RI	(37, 38)
HgCl <sub>2</sub>	IN	(6)	Mo(CO) <sub>6</sub>	RI	(37)
HgBr <sub>2</sub>	IN	(6)	Fe(CO) <sub>5</sub>	RI	(39)
HgI <sub>2</sub>	IN	(62)	Co(CO) <sub>4</sub> H	I	(40)
GaCl <sub>3</sub>	R	(11)	SiD <sub>4</sub>	IN	(19)
H <sub>2</sub> O <sub>2</sub>	R	(12)	SiHD <sub>3</sub>	IN	(19)
Al <sub>2</sub> Cl <sub>6</sub>	IN	(7)	SiH <sub>3</sub> D <sub>2</sub>	IN	(19)
PI <sub>3</sub>	R	(8)	(SiH <sub>3</sub> ) <sub>2</sub> O	RI	(57)
AsI <sub>3</sub>	R	(8)	(SiD <sub>3</sub> ) <sub>2</sub> O	RI	(57)
S <sub>2</sub> Br <sub>2</sub>	R	(9)	(C <sub>2</sub> H <sub>5</sub> )SiCl <sub>3</sub>	RI	(58)
Se <sub>2</sub> Cl <sub>2</sub>	R	(9)	(CH <sub>3</sub> ) <sub>3</sub> B	I	(42)
Se <sub>2</sub> Br <sub>2</sub>	R	(9)	(CH <sub>3</sub> ) <sub>4</sub> Sn	RI	(43)
BF <sub>2</sub> Cl	IN	(10)	CHOF	RI	(13)
BFBBr <sub>2</sub>	IN	(10)	CDOF	RI	(13)
BCl <sub>3</sub> Br	IN	(10)	CHI <sub>3</sub>	R	(18)
NO <sub>2</sub> F	RI	(14)	CF <sub>3</sub> CN	RIN	(26)
B <sub>2</sub> O <sub>3</sub>	I	(17)	CF <sub>3</sub> NO	I	(27)
OsO <sub>4</sub>	RIN	(20, 21)	CF <sub>3</sub> NO <sub>2</sub>	I	(28)
GaCl <sub>4</sub> <sup>-</sup>	R	(22)	CCl <sub>3</sub> NO <sub>2</sub>	I	(28)
BH <sub>4</sub> <sup>-</sup>	R	(23)	CBr <sub>3</sub> NO <sub>2</sub>	I	(28)
P <sub>2</sub> H <sub>4</sub>	I	(24)	C <sub>2</sub> Br <sub>4</sub>	IN	(29)
P <sub>2</sub> D <sub>4</sub>	I	(24)	(CHCl <sub>3</sub> ) <sub>2</sub>	I	(31, 32)
B <sub>3</sub> H <sub>6</sub>	I	(25)	(CHBr <sub>3</sub> ) <sub>2</sub>	I	(31)
B <sub>3</sub> H <sub>9</sub>	I	(25)	C <sub>6</sub> D <sub>6</sub>	I	(44)
B <sub>10</sub> H <sub>14</sub>	I	(25)	CH <sub>3</sub> CCD <sub>2</sub>	RI	(45)
C <sub>2</sub> H <sub>4</sub> O	RI	(46)	(CD <sub>3</sub> CO) <sub>2</sub>	I	(52)
C <sub>2</sub> D <sub>4</sub> O	RI	(46)	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	I	(53)
CH <sub>3</sub> CHO	RI	(16, 49)	(CH <sub>3</sub> ) <sub>2</sub> CH	RI	(54)
CH <sub>3</sub> CDO	RI	(16, 49)	(CH <sub>3</sub> ) <sub>2</sub> CD	RI	(54)
CHO <sub>2</sub> H	I	(47, 48)	CH <sub>3</sub> NH <sub>2</sub>	IN	(41)
CHO <sub>2</sub> <sup>-</sup>	RI	(15)	(CH <sub>3</sub> ) <sub>2</sub> NH	IN	(41)
CH <sub>2</sub> O	I	(16)	(CH <sub>3</sub> ) <sub>3</sub> N	IN	(41)
(CO <sub>2</sub> H) <sub>2</sub>	RIN	(50)	<i>o</i> -C <sub>6</sub> H <sub>4</sub> ClF	RI	(55)
(CO <sub>2</sub> ) <sub>2</sub> <sup>-</sup>	RIN	(15, 50)	<i>p</i> -C <sub>6</sub> H <sub>4</sub> ClF	RI	(56)
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	RI	(15, 51)	<i>p</i> -C <sub>6</sub> H <sub>4</sub> BrF	RI	(56)
(CH <sub>3</sub> CO) <sub>2</sub>	I	(52)	<i>p</i> -C <sub>6</sub> H <sub>4</sub> IF	RI	(56)

\* R=Raman spectrum; I=infrared spectrum; N=normal coordinate computation.

& Hornig (59) for benzene itself. These studies crown the work of many previous investigators and demonstrate the labor involved in establishing a complete assignment for even a moderately simple molecule. Similar considerations apply to the work of Lord & Nolin (46) on ethylene oxide and of Evans & Bernstein (49, 54) on acetaldehyde and isobutane. The methyl derivatives of ammonia (41), biacetyl (52), acetyl methyl carbinol (53), and various aldehydes, acids and carboxylates (15, 16, 47, 48, 50, 51) have also been treated in considerable detail. Siloxane and siloxane- $d_8$  have been studied by Lord, Robinson & Schumb (57) and vinyl silicon trichloride by Shull, Thursack & Birdsall (58). These molecules are of interest because of their relationship to silicone polymers. It is interesting to note that the data for the former molecules suggest that the Si-O-Si group is linear or nearly so. Other metal-organics for which complete assignments have been made are  $\text{Sn}(\text{CH}_3)_4$  (43) and  $\text{B}(\text{CH}_3)_3$  (42). The barrier to internal rotation of the methyl groups in the latter molecule was computed as 750 or 1640 cal. per mole for structures with or without a threefold axis of symmetry.

A number of interesting studies have been made of inorganic molecules and ions. These have been fruitful in yielding information about structure and the nature of the chemical bonds involved. Klemperer and co-workers (3, 6, 7, 62) and Dows & Porter (17) have applied infrared emission techniques to this area. These data suggest that compounds such as  $\text{HgCl}_2$  are linear while support is found for the trigonal bipyramid ( $D_{3h}$ ) structure of  $\text{B}_2\text{O}_3$ . Stammreich and co-workers (8, 9, 18) have obtained the Raman spectrum of various light-sensitive molecules by using an exciting source in the red or near infrared region of the spectrum, and King & Lippincott (39) have applied similar ideas to  $\text{Fe}(\text{CO})_5$ . Woodward, Garton & Roberts (11) have found that the Raman spectrum of fused  $\text{GaCl}_3$  is in close agreement with the spectrum of  $\text{GaCl}_4^-$  in an aqueous solution (22). Thus, the molecule is to be considered as  $[\text{Ga}^+] [\text{GaCl}_4^-]$  rather than a structure involving Ga-Ga bonds. The  $\text{OsO}_4$  molecule has been shown to be tetrahedral (20). Since the Raman spectrum of aqueous solutions of the isoelectronic perrhenate and tungstate ions ( $\text{ReO}_4^-$  and  $\text{WO}_4^{2-}$ ) are very similar, it is concluded that they also are tetrahedral (rather than being octahedral due to coordination with water molecules, as had been suggested). The nature of the osmium-oxygen bonds have been discussed (20, 21) but problems remain regarding this molecule (21). Rather difficult molecules have been well handled in the work of Morgan, Staats & Goldstein (13) on  $\text{HCOF}$  and  $\text{DCOF}$ , and of Dodd, Rolfe & Woodward (14) on  $\text{NO}_2\text{F}$ . A comprehensive study of the Raman spectrum of pure liquid hydrogen peroxide and its aqueous solutions has been carried out by Taylor & Cross (12). This work yields important information regarding the interaction of the molecules in the liquid state and in solution. Inorganic complex ions have continued to receive attention. Among the simpler ions (33, 34, 35) studied, the thorough treatment of the tetracyanoplatinate (II) ion by Sweeney *et al.* (35) should be noted.

In contrast to the essentially completed status enjoyed by benzene is the

work on the vibrational frequencies of the metal carbonyls and their derivatives. Here the studies are in the earlier phases where the prominent frequencies and the nature of the modes of vibration are being established. These serve as good examples of this phase of molecular spectroscopy at work, for the object is to determine the nature of the chemical bonds involved in this interesting class of molecules. Jones (36) has extended the infrared spectrum of  $\text{Ni(CO)}_4$  to  $38\ \mu$  and modified the earlier assignment of Crawford & Cross (63). While this assignment must be nearly correct, at least one major feature is missing since a wholly satisfactory explanation of the overtone and combination bands observed in the infrared is not obtained. King & Lippincott (39) have observed three of the Raman active fundamentals of  $\text{Fe(CO)}_5$ . Combining these with the infrared data of Sheline & Pitzer (64), frequencies were assigned to all eighteen fundamentals assuming three coincidences and estimating six other values. An examination shows, however, that this assignment also does not satisfactorily account for the infrared overtone and combination bands. King & Lippincott point out that their data support the view that the metal-carbon and carbon-oxygen bonds are essentially single and triple bonds, respectively. The view that both kinds of bonds have considerable double bond character rests primarily upon electron diffraction data (65, 66) which show that the CO bonds are longer than in carbon monoxide and that the metal-carbon bonds are shorter than the sum of the atomic radii. It may be that a new idea relating to the structure of these molecules is required to bring these apparently conflicting types of data into harmony. Shuffer, Sternberg & Friedel (38) have pointed out that the infrared spectra of  $\text{Cr(CO)}_6$  and  $\text{Fe(CO)}_6^{++}$  (67) show that all CO bonds are equivalent and indicate a regular octahedral structure for these and other hexacarbonyls. Hawkins *et al.* (37) have made a complete frequency assignment for  $\text{Cr(CO)}_6$  and  $\text{Mo(CO)}_6$ , making full use of the infrared overtone and combination bands. While some uncertainty is to be attached to the low frequency assignments, a noteworthy feature of this work is the placing of the symmetric CO stretching frequency just above  $2100\ \text{cm}^{-1}$ . The presence of  $\text{C}^{13}\text{-O}$  stretching frequencies in the spectra of metal carbonyls has been discussed (36, 38).

Edgell, Magee & Gallup (40) have studied the infrared spectrum of  $\text{Co(CO)}_4\text{H}$ , the catalyst in the oxo process. Because the  $703\ \text{cm}^{-1}$  band is the highest observed frequency associated with hydrogen, the model where the hydrogen atom is attached to the oxygen atom (66) is eliminated. The hydrogen atom is placed on the  $\text{C}_3$  axis of the tetrahedron because of the number of CO frequencies assigned, but could also lie on a  $\text{C}_2$  axis if accidental degeneracy occurs. It is suggested that the hydrogen atom is bound to CO groups as well as to the cobalt atom, but the relative strength of these two kinds of bonding is considered a matter for further study. Edgell & Wilson (67) have reported on their study of  $\text{Co(CO)}_4\text{D}$  which confirms the assignments made for  $\text{Co(CO)}_4\text{H}$ . Neither extreme limit of the model appears as satisfactory as an intermediate one.

*Theory.*—As pointed out above, one of the primary applications of spectral data is to determine the intramolecular forces and atomic displacements. A major difficulty lies in the fact that there are more force constants than there are vibrational frequencies for polyatomic molecules. As a result, there are, in fact, an infinite number of force constant sets which will reproduce the data. Two methods have long been used to circumvent this difficulty. These involve the use of isotopic molecules and the transfer of constants from one molecule to another containing the same bond. The first method makes use of the well established fact that isotopic substitution leaves the force field invariant and the second assumes that a bond is independent of its environment. The limitations of the second assumption are generally understood.

That pitfalls are sometimes involved in the first method has been less clearly recognized. For example, Glockler & Tung (68) have plotted all the force constants that reproduce the  $\text{H}_2\text{O}$  frequencies as ellipses. The force constants selected appear where the ellipses for  $\text{D}_2\text{O}$  cross those for  $\text{H}_2\text{O}$ . But the difficulty stems from the fact that the ellipses for  $\text{D}_2\text{O}$  are approximately superimposable on those for  $\text{H}_2\text{O}$ . Small changes make a large difference in the crossing point of the two nearly parallel lines. The same situation can apply in other molecules. Thus, when anharmonic corrections are not made and errors in frequency exist, the resultant error in certain force constants can be rather large. Most force constants have been evaluated solely under the criterion that they reproduce observed frequencies. This is not sufficient of itself to guarantee accuracy and may result in a distorted picture of the actual intramolecular forces and the amplitudes of vibration.

Two general methods may be used to improve the accuracy of force constants, viz, the use of experimentally determined centrifugal distortion constants and Coriolis constants. Pierce (70) has combined the infrared frequencies of ozone with the distortion constants obtained from microwave spectroscopy to determine the force constants. This parallels the earlier work of Kivelson (69) on  $\text{SO}_2$  and promises to provide a sensitive method where it can be applied. Classical examples of the application of Coriolis constants in defining force fields may be found in the work of Dennison and co-workers (71, 72) on methane and ethane. Unfortunately, this method has not been applied in many cases.

Two recent developments will improve this situation for the future. To obtain Coriolis constants has required the resolution of the fine structure of perpendicular bands. And this, in practice, has meant a limitation to molecules which have none but hydrogen or deuterium atoms off the principle axis of symmetry. Edgell & Moynihan (73, 74) have recently studied the influence of Coriolis coupling on the shape of infrared bands. For spherical top molecules, it is found that the Coriolis constant  $\zeta$  can be computed from the separation  $\Delta\nu$  between the absorption maxima of the P and R branches through the equation

$$\Delta\nu = (2kT/\pi^2c^2I)^{1/2}(1 - \zeta).$$

No simple closed expression was possible for symmetric rotors. However, these authors used a digital computer to prepare an atlas of band contours covering the range of  $\zeta$  and the domain of the oblate rotor. Here also the PR maxima separation could be correlated with values of  $1-\zeta$ . Thus, Coriolis constants can be obtained for heavier molecules where the fine structure of the bands cannot be resolved and, hence, should be more generally available for force field calculations.

In the second development, Meal & Polo (75, 76) have considered the properties of the Coriolis constant matrices and have developed general methods of obtaining relations among these constants which depend only upon atomic masses and geometry (such as the sum rules). More pertinent to this discussion, these authors have established convenient relations between the Coriolis constants and the force constants and have indicated a method for the calculation of Coriolis constants along with the normal coordinate treatment in terms of any chosen set of internal coordinates. As a result, normal coordinate treatments in the future will have a ready means of utilizing whatever data are available on Coriolis constants. In other developments relating to normal coordinate treatments, Shimanouchi has indicated a method for obtaining a good first approximation to the characteristic vector when the indirect expansion method based upon the Hamilton-Cayley theorem is used for large secular equations (77); he has also derived general formulae for inverse kinetic energy matrix elements for in-plane vibrations of planar molecules (78).

Polo (79) has discussed the  $t$  or displacement vectors introduced by Halverson & Francel (80) and showed how these may be used to compute the kinetic energy matrix  $G^{-1}$ . Dowling (81) has given the  $s$  vectors for the torsional and out-of-plane vibrations for ethylene type molecules.  $F$  and  $G$  matrix elements have been obtained and calculations carried out for 57 such vibrations in 19 molecules. Force constants have been computed for the bromosilanes (82), and for 14 tetrahedral  $XY_4$  (83), and for 9 planar  $XY_3$  (84) molecules or ions using Raman data. A special force field has been proposed for out-of-plane motions of planar molecules (85). Normal coordinate treatments have been carried out for a number of other molecules as indicated in Table 1. Attention should be drawn to the work of Smith & Linnett (86) on nonlinear triatomic molecules. The problem of obtaining an unique set of constants is discussed and general conclusions drawn regarding the meaning of the force fields present in this class of molecules.

In other contributions to gas phase theory, Bauman (87) has demonstrated that the selection rules for a freely rotating ethane-type molecule should be those of the  $D_{3d}$  group rather than  $D_{3h}$ , Bernstein (88) has applied the vibrational sum rules to the halogenated ethylenes, and Kimura & Kimura (89) have indicated an approximate method for computing mean square amplitudes of vibration.

Several interesting papers have appeared during the last year dealing with

various aspects of the theory of crystal spectra. Hexter & Dows (90) have discussed the effect of molecular libration about axes perpendicular to those of the transition moments of molecular vibration. This results in deviations of the dichroic ratios from those predicted by the oriented gas model as have been observed for iodoform, brucite, and other molecules. From a measurement of this effect and a knowledge of the libration frequencies, the orientation of molecules or functional groups in crystals can be determined. The theory of the Raman effect in crystals has been modified by Theimer (91), who makes a distinction between electrons localized in atomic or molecular orbitals and those in delocalized crystal orbitals. Selection rules are obtained which agree with experimental results for calcite and similar crystals. Temperature effects are also discussed. Using classical dispersion theory, Haas (92) has explained various anomalies which appear in the vibrational spectra of crystals. These include the differences between the frequency of the Raman shift and that of the maxima in infrared absorption, reflection and emission spectra as well as the very broad reflection bands, all of which occur when a fundamental gives rise to strong absorption.

The measurement of the intensity of narrow infrared lines or of narrow Q branches has always involved difficulties. In a significant development, Penner & Aroeste (99) have proposed a "curve of growth" method to meet this problem. When spectral lines can be described by a combination of Doppler and Lorentz broadening, a simple experimental procedure permits the estimation of line profile and absolute intensity. Kaplan & Eggers (60) have applied this idea to the measurement of the intensity of the Q branch of the  $15\mu$  band of  $\text{CO}_2$  and find a 25 per cent increase in band intensity over that obtained by the Wilson-Wells extrapolation. The band intensities in methylene bromide and iodide were measured by Singh & Straley (93),  $\text{BF}_3$  by McKean (94), and  $\text{NH}_3$  and  $\text{PH}_3$  by McKean & Schatz (95). Effective bond moments and their bond length derivatives were computed. The effect of the lone-pair electrons was included in the work on  $\text{NH}_3$  and  $\text{PH}_3$ . Depolarization measurements were made for the symmetric Raman lines of  $\text{CBr}_3\text{X}$  molecules by Krupp, Ferigle & Weber (97) and compared with computations, as was done for similar molecules by Weber & Ferigle (96). Agreement is obtained for stretching but not bending modes.

It is now well established that bond dipole moments and their bond length derivatives vary with the symmetry class of the vibration for the same molecule. These findings indicate the limitations of the effective bond moment and effective bond polarizability theory. Bonding theory suggests that derivatives such as  $\partial\mu_i/\partial\theta_{ij}$ , etc., which are neglected in current treatments, are not negligible; and it is inevitable that they will be eventually introduced into these treatments. Meanwhile, the task of laying out the foundation continues.

A very complete and thorough measurement of the infrared transmission of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and their combination in synthetic atmospheres has been made



by Howard, Burch & Williams (100 to 104). The intensity and depolarization factor of the Raman lines of liquid  $\text{CS}_2$  and its solutions with cyclopentane have been measured by Evans & Bernstein (98). The relative intensity of the forbidden bands  $\nu_2$  and  $\nu_3$  decrease rapidly with dilution. It might be pointed out at this point that Gallup (61) explains the side bands of  $\nu_2$  in the infrared as arising from the libration of the molecule with the hindering potential furnished thru intermolecular interaction. Legay & Cabannes (105) have measured the dispersion in the infrared bands of HCl and obtained the constants in the dipole moment expansion. More complex molecules have also been treated. In an interesting paper by Russell & Thompson (106), the intensity of the first overtone band of the NH group has been studied for a number of molecules. By comparing these data with previous work on the fundamentals, numerical functions are obtained for the dipole moment as a function of bond length in the different compounds which reveal interesting correlations with ionic character. Tsubomura (107) has obtained the intensities of the free and hydrogen bonded OH bands in various molecules. They find that the major factor increasing the intensity of the intermolecularly bonded OH bands is the charge transfer through the hydrogen bond and an explanation is offered for the weakness of the bands in chelate compounds. The relationship between infrared intensities in the gaseous and liquid state has been considered by Polo & Wilson (108) and Jaffe & Kimel (109) and the temperature effect in solution by Hughes, Martin & Coggeshall (110). White & Howard (111) have measured the 90 and 50 per cent intensity widths of a number of liquid compounds and considered the resolution required to obtain data which is independent of small changes in spectral slit width and is interchangeable between different instruments.

*Larger molecules.*—The understanding of the vibrational spectra of larger molecules rests upon the accumulated data for smaller molecules. A great amount of work is being done in this area and it is unfortunate that much of it can not be discussed here. A description of the current state of affairs might be one of transition between a period largely devoted to the accumulation of data and their empirical correlation with the presence of various molecular groups and structural units, and, one devoted to the detailed interpretation of the spectra. The first period has nearly come to an end and the second is well begun. The area may be divided into four parts: (a) the calculation of vibrational frequencies and force constants, (b) the assignment of vibrational frequencies, (c) the study of the effects of environment on molecular or group frequencies and intensities, and (d) the applications to problems of chemical interest.

Sheppard (112) has collected together the values of the symmetrical deformation frequency of the methyl group when it is attached to atoms in groups four to seven of the periodic table, and has discussed the variation in terms of electronegativity and position in the table. The frequency changes are reflected in force constant variations. Nakagawa & Mizushima (113)

have carried out a normal coordinate treatment of the  $\text{CH}$ ,  $\text{CH}_2$ , and  $\text{CH}_3$  deformation frequencies in various organic compounds and of the  $\text{NH}_3$  deformation frequencies in metal amines. The approximation made was to consider only the immediate atoms attached to the groups in question and to retain only diagonal terms in the  $G$  and  $F$  matrices.

Another approach to the frequency computation problem in larger molecules is to transfer force constants from smaller molecules. Brown & Sheppard (114) use the force constants of ethylene and compute the out-of-plane frequencies for molecules in which heavy substituents replace one or more hydrogen atoms. The general applicability of this method for determining characteristic frequencies of other systems is discussed. The perturbation treatments of Higgs (115, 116) and Edgell & Riethof (117) have laid a foundation for the normal coordinate treatment of larger molecules. A very useful extension of this work has been made by King & Crawford (118) for the case where the coupling between the group and skeletal modes is weak. These conditions lead to the use of effective masses for the group atoms in the treatment of the skeletal modes and should be especially useful with methyl, methylene and similar groups. Liang, Krimm & Sutherland (119) have given an excellent discussion of the calculation of the skeletal frequencies, the selection rules, and the experimental methods applicable to polymer molecules. These methods have been applied to polyethylene (120), polytetrafluoroethylene (121), and polyvinyl alcohol (122). Ferguson (143) has discussed polyethylenes and long chain  $n$ -paraffins. The influence of the coupling of various modes upon the dichroism of crystalline acetanilide has been discussed by Abbott & Elliott (124), and, upon the intensity of the  $10\mu$  band in substituted benzenes by Randle & Whiffen (123). Dichroism in partly oriented polymers has been treated by Beer (125).

A great deal of careful work has been done on frequency assignments. Attention should be called to the study of deuterated esters by Nolin & Jones (126, 127) and to further contributions useful in the recognition of steroids (128). Amides and polypeptides have been discussed in some detail (129 to 133). Transition metal complexes are receiving considerable attention (134 to 138) with most of the identified bands being assigned to the complexing units. An interesting study of the water of crystallization in calcium and strontium chlorides has been made (150). Aromatic compounds of various types have been studied (139 to 142) as well as tetraphenyl porphines (144), tertiary amine oxides (147), ozonides (145), and triphenyl hydrazine (146). The bands associated with the OH or OD vibration in various chelated, unsaturated hydroxycarbinols have been assigned (148). Site-group selection rules have been applied to the interpretation of the spectrum of a hexathiaadamantate (149).

Knowledge is rapidly increasing with regards to the effect of molecular environment on group frequencies and intensities, and this promises to be of utility not only in analysis but also in the field of physical organic chemistry

and possibly in reaction kinetics. Bellamy (151) has discussed a number of cases in which the frequency of mass-insensitive vibrations can be correlated quantitatively with inductive and resonance effects and with the physical and chemical properties usually associated with them. An interesting attempt is made at unification. Chatt, Duncanson & Venanzi (152) have studied the spectra of *trans* platinum (II) complexes containing both a primary or secondary amine and one (other) ligand selected from a large series. Strong inductive effects are transmitted across the platinum atom from the ligand to the NH bond and the donor capacities of various atoms are correlated with their electronegativity. However, it is the tendency to coordinate by double bonds which is related to the *trans* directing effect and not the electronegativity of the ligand.

It has been found by Kross & Fassel (153) that the frequency of the symmetric mode of vibration of the nitro group in *para* substituted nitrobenzenes yields a straight line when plotted against molecular dipole moments or Hammett's sigma function. The carbonyl frequencies of oxindale vary with the substituents in the benzene ring according to their sigma value, the effect being transmitted thru the NH group (154). The positive shift of the frequency of an out-of-plane CH bending mode in *mono* and *para* disubstituted benzenes is correlated with the electrophilic nature of the substituents (155). This is shown to be consistent with the decreased ease of orbital following caused by the withdrawal of  $\pi$  electrons from the ring. Shifts in the CO frequency of substituted acetophenones and benzoic acids have been related to the CO bond order computed by a molecular energy level scheme (156).

The role of the solvent in modifying frequencies and intensities has been discussed for dichlorocyclohexane by Yoshino (159) and for various cyano- and nitrobenzenes by Lippert (157, 158). Hydrogen bonding has been investigated in a number of systems (160 to 165). Attention should be directed to the careful study of aliphatic alcohols by Stuart & Sutherland (161), and of the dimethyl ether-HCl(HBr) system by Vidale & Taylor (164) as well as to the correlation of the stretching frequency with hydrogen bond distance in crystals shown by Pimentel & Sederholm (165). The broadening of certain bands in hydrogen bonded systems is attributed by Frisch & Vidale (234) to coupled anharmonic vibrations and a classical mechanical treatment is carried out. The role of steric effects in  $\omega$ -chloroacetophenones has been treated by Bellamy, Thomas & Williams (166) and in ephidine and related compounds by Kanzawa (167, 168). Coordination effects have also been studied in certain metal complexes (169, 170).

#### ROTATION SPECTRA

Some of the studies dealing with the analysis of infrared rotation-vibration bands, the rotational Raman effect and microwave spectra will be discussed in this section.

The last several years have seen the development of more sensitive infrared detectors [PbS, PbTe], the availability of high quality gratings, and improvements in optical arrangements (double passing, etc.). The resultant increase in resolution has prompted the reexamination of the spectra of molecules first studied some twenty years ago. While the chemist may be inclined to describe these molecules as simple, such an adjective cannot be applied to the dynamical interactions which are responsible for the details of their band structures. Already, the results of the second order perturbation treatment of the interaction of rotation and vibration are proving inadequate for a complete description of the findings, and a start has been made on extending the theory to the fourth order by Goldsmith, Amat & Nielsen (171). The recent measurements provide dynamical and structural parameters of increased accuracy. This is also true of the data provided by microwave and Raman spectroscopy. These data show interesting effects of molecular environment on bonds whose quantitative, and sometimes qualitative, explanation stands as a challenge to theoretical chemistry.

The influence of Fermi resonance on centrifugal distortion and *l*-type doubling in a linear molecule has been treated theoretically by Amat, Goldsmith & Nielsen (175, 176) and applied to measurements on the 100, 020 and 101, 021 diads of carbon dioxide [Nielsen *et al.* (179)]. The *P* and *R* structure of the  $15\mu$  band of  $\text{CO}_2$  has been resolved to  $J=60$  and the molecular constants evaluated [Rossmann, Rao & Nielsen (177)]. Resolution of three bands in  $\text{CS}_2$  lead to values for  $B_0$ ,  $D_0$  and  $r_0$  (178). Dagg & Thompson (172) have measured some bands in HCN and DCN, resolving not only the *P* and *R* branches but also splitting the *Q* branches in some cases. Evaluation of the  $\alpha$  lead to equilibrium values for the rotational constants and interatomic distances. A dimeric form of HCN is proposed to explain a band near  $5\mu$ . A complete determination of the anharmonic constants for these two molecules has resulted from a study of 22 bands of HCN and 18 of DCN by Allen, Tidwell & Plyler (173). A third order resonance between levels of the type  $(v_1, v_3, v_3)$ ,  $(v_1+3, v_2, v_3-2)$  was shown to be present. Rank *et al.* (180) have measured the *l*-type doublets in nine  $\pi$ - $\pi$  bands of  $\text{N}_2\text{O}$  between  $1.5$  and  $2.4\mu$  and found that the doublet separations depend upon the vibrational quantum numbers for  $v_1$  and  $v_3$  as well as  $v_2$ . The theory was extended accordingly. The extremely high resolution of  $0.03\text{ cm}^{-1}$  at  $4330\text{ cm}^{-1}$  was obtained. Twelve previously unreported bands have been studied under high resolution and analyzed [Plyler, Tidwell & Allen (182)]. A precise value for  $v_3$  is obtained. Resolution of the  $v_2$  band at  $17\mu$  has been achieved and molecular constants determined by Lakshmi, Rao & Nielsen (181). High resolution studies have also been carried out on NO (183) and  $\text{NO}_2$  (184).

Attention should be directed to the very complete study of deuterated water vapor between  $1.25$  and  $4.1\mu$  by Benedict, Gailar & Plyler (185). Forty five hundred lines were measured and analyzed as arising from ten

bands of  $D_2O$  and nine from  $HDO$ . A table of energy levels is given and the vibration-rotation constants are derived. Dalby & Nielsen (201) have studied the  $6\mu$  region of water. Allen *et al.* (186) find that their observations on  $H_2S$  between  $3.6$  and  $4.5\mu$  are to be understood in terms of the overtone of  $\nu_2$  and the  $\nu_1$  fundamental. The results do not agree with the previous assignment of the high frequency region of this interval to  $\nu_3$  in analogy to water. Preliminary values for the molecular structure of  $H_2Te$  have been obtained by Rossmann & Straley (187) from the band analysis in the  $5$  and  $11.5\mu$  regions. Acetylene and its deuterated analogs continue to be the subject of careful and detailed study. Overend & Thompson (188) obtained the  $\alpha$  and equilibrium values of the rotational constants and molecular dimensions from their study of  $C_2HD$ . Anharmonic constants were evaluated for  $C_2D_2$  by Allen, Blaine & Plyler (190). The effect of Fermi resonance on centrifugal constants in the  $\nu_4 + \nu_6$  band of acetylene has been treated [Coburn, Rao & Nielsen (189)] and its role in the spectra of  $C_2HD$  and  $C_2D_2$  noted (188, 190).

Other high resolution infrared studies which should be noted include the molecules ketene (191), diazomethane (192),  $ClO_3F$  (193), and  $HF$  (194). This author was intrigued by the possibilities associated with a study such as that of the  $9.6\mu$  band of atmospheric ozone from the Jungfraujoch in Switzerland (195). The moderate resolution available from double passed prisms or gratings in small instruments makes it possible to resolve some of the band structure of molecules with small moments of inertia. Studies of this kind have included  $CD_3F$  (196, 197),  $SnH_4$  (198),  $Ge_2H_6$  (199), and the silyl halides (200). High resolution studies of the rotational Raman spectra of allene, allene- $d_2$  and allene- $d_4$  have been made by Stoicheff (202), of benzene- $d_3$  by Langseth & Stoicheff (203), and of solid and liquid  $H_2$  by Allin, Feldman & Welsh (204). Molecular parameters are computed.

Among the molecules for which structural information has been obtained this year by the study of rotational transitions in the microwave region, mention should be made of formic acid [Wertheimer (205); Erlandsson (206)], chloroform [Wolfe (207)], pyrrole [Bak *et al.* (208)], trimethyl bromo and iodo silane [Ollom *et al.* (209); Rexroad *et al.* (210)], nitrogen dioxide [Bird (211)], and hydrogen selenide [Jache, Moser & Gordy (212)]. The structure of ozone seems to be settled at last by the definitive work of Hughes (213) and the rotational lines of a number of linear molecules have been measured with high precision in the region between  $0.8$  and  $2$  mm. by Burrus & Gordy (214). Cox & Gordy (215) have measured the Zeeman effect of some linear and symmetric tops and computed the  $g$  factors. Transitions between the  $\lambda$ -type doublets of the rotational states of the  $OH$  and  $OD$  radicals have been observed by Dousmanis, Sanders & Townes (216) using Zeeman modulation. The results are interpreted in terms of Van Vleck's theory for such energy states with extensions.

Burkhard (217) has given a general theory of hindered rotation for a rigid symmetric and rigid asymmetric group rotating about a common axis,

and Kivelson (218, 219) has treated the effects due to the inclusion of vibrational motion. Microwave spectroscopy offers several possibilities for the study of internal rotation. One of the most recent and promising developments involves the detection of the splitting of certain rotational lines by this motion. The torsional levels of a symmetric rotor like the methyl group are split into two components (the *A* and *E* energy levels) by the tunnelling effect and these states have slightly different effective moments of inertia for over-all rotation. As a result, the rotational lines are doubled. The separation is very small but increases with *J*, torsional quantum state, and decreasing barrier height. Since the splittings depend upon barrier height, these can be used to evaluate it where the effect can be observed. A full report on this work has not yet appeared but the method has been discussed by Wilson (220) and some preliminary results reported (221, 222). Readers are also referred to the abstracts of several papers using this method which were read at the Symposium on Molecular Structure and Spectroscopy, Ohio State University, June, 1956.

#### IMPROVEMENTS IN TECHNIQUES

Steady advances continue to be made in spectroscopic techniques. Several laboratories have now replaced the Littrow mirror in small prism infrared spectrometers by gratings. If the prism is also removed, the paraboloid should be replaced with one having the proper off-axis angle. If the prism remains, no change need be made in the monochromator. Both methods have advantages and disadvantages. Resolutions of the order of  $0.3\text{ cm}^{-1}$  at  $2.5\mu$  and  $0.5\text{ cm}^{-1}$  at  $15\mu$  have been achieved. Although one grating may be used in various orders to cover this region, maximum performance is obtained only at those wavelengths which fall near the blaze angle. This is not a major deterrent since such gratings are reasonable in cost, and it may be expected that they will gradually become available with suitable blaze angles to provide excellent coverage not only for this region but also for longer wavelengths. This increased performance is achieved at the sacrifice of some ease of operation associated with the elimination of overlapping orders. Both filters and foreprisms have been used for this purpose. While the former are especially suitable for the near infrared, the latter provide a greater flexibility of operation. Thus, Plyler & Acquista (224) have extended small instrument operation to  $125\mu$  from the present prism limit of  $50\mu$ . Commercial grating instruments are becoming available (225, 226). A zirconium arc source has been developed for use with a microscope attachment which gives an increase in energy over a globar of 2.25 at  $14\mu$  and 4 at  $4\mu$  (227). Those who have had the problem of reducing bulky infrared charts for reports and for easier cataloging, reference and comparison, will find interesting the  $8\frac{1}{2}\times 11$  inch tracing produced by the recording system described by Olsen, Johnsen & Pierson (228). Crosswhite & Fastie (229) have described a new slit mechanism which is particularly suited for Ebert monochromators,

while Golay (223) has discussed the performance characteristics of a number of spectrometric systems, some new and some old. It is difficult or impossible to obtain the Raman spectra of colored or photosensitive materials with conventional mercury sources. Stammreich (230) has described experimental techniques for exciting Raman spectra in the red and near infrared region of the spectrum, and King & Lippincott (231) have used sodium vapor lamps for similar purposes. Becker & Pimentel (232) describe matrix isolation methods for trapping free radicals or reactive molecules for spectroscopic study. The principles of design, construction and operation of equipment for growing thin sections of single crystals for infrared study have been treated by Zwerdling & Halford (233).

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## EXPERIMENTAL MOLECULAR STRUCTURE<sup>1</sup>

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There has been a large number of structure determinations in the past twelve months. For this review the literature has been searched as far as possible up to the middle of December, 1956, and, while there are doubtless some omissions, it is hoped these are few. The number of determinations, divided among the various experimental methods, is listed in Table I. Metals and alloys (whose structures have almost always been found by means of x-rays) are excluded, as well as the many interesting investigations which have resulted only in a determination of, or a restriction on, the molecular symmetry.

TABLE I

THE NUMBER OF STRUCTURAL DETERMINATIONS DIVIDED AMONG THE VARIOUS EXPERIMENTAL METHODS\*†

RR	VR	UV	MW	NMR	ED	ND	XRD
3	15	2	11	3	14	4	189

\* RR=rotational Raman spectrum; VR=infrared vibration-rotation spectrum; UV=ultraviolet spectrum; MW=microwave spectrum; NMR=nuclear magnetic resonance spectrum; ED=electron diffraction; ND=neutron diffraction; XRD=x-ray diffraction.

† In order to qualify for this table at least one bond length must have been obtained from the determination. The table includes structures obtained by VR, MW, ED, and XRD methods in which some bond lengths were assumed so as to obtain others. The number of XRD results includes those that gave solely interionic distances.

The great majority of structural determinations was carried out by x-ray crystallography. It is inevitable at the present time that this should be so, since all substances can be obtained in a solid form, whereas not all can be obtained as gases. However, it is well known that the accuracy of x-ray analyses is less than that of spectroscopic methods, and it is obviously of great importance to increase the accuracy of crystallographic determinations if possible. This review, instead of listing the many recent structural determinations, will be divided into two parts. The first part will discuss the accuracy of crystal structure determinations (1) and the efforts which have been made to improve them. The second part will be concerned with a few molecules which can apparently have different configurations in different circumstances.

<sup>1</sup> The survey of literature pertaining to this review was completed in December, 1956.



## THE ACCURACY OF X-RAY CRYSTAL ANALYSIS

With care, cell dimensions can be determined with an accuracy equal to, or better than, the best microwave results, and there are a number of cases in which an interatomic distance depends directly on the unit cell dimensions. Obvious examples are the ionic crystals with cubic symmetry such as sodium chloride. A recent illustration of such determinations of interionic distances is the work on the alkaline-earth sulphides (2). However, the method is not solely restricted to finding interionic distances. The lengths of pure covalent bonds, such as those found in diamond and silicon, are also a function of the cell side alone, and hence can be found with great accuracy.

In general, however, it is not sufficient merely to find the positions of the diffracted beams, since the determination of an atomic position is based partly on an estimate of the intensities of these beams. In the vast majority of current x-ray crystal analyses the intensities are measured photographically. The standard deviation of the intensities observed in this way is of the order of 10 to 20 per cent. This is a major source of error in present-day crystallographic determinations. In principle it is possible to reduce this error to 1 to 2 per cent by the use of counter techniques, but in fact very few structural determinations have been based on intensities obtained with counters. The reason for this is that at present it takes much longer to obtain the same number of intensities with a counter than it does photographically. The error in a derived quantity which is based on observations subject to random errors is inversely proportional to the square root of the number of observations. Thus it has been the policy for the last 10 or 15 years, when accuracy of atomic positions is of prime importance, to obtain as many measured intensities as possible. Since the accuracy with which the intensity of a diffracted beam can be measured is not constant over the whole range of observation, this policy is open to objection; but on the whole the policy is a good one, and it will remain a good one until intensities can be obtained with "100 per cent accuracy." The phrase "100 per cent accuracy" is meant to imply that the proportional error in the observed intensities is no greater than in the other quantities involved in crystallographic calculations.

Apart from random errors, there are various sorts of systematic errors. With one exception these errors are well understood and can be allowed for, although the corrections needed are sometimes laborious to apply. Errors attributable to extinction are more obscure, and the method proposed by Chandrasekhar (3) for dealing with such errors is of great interest. In the past, extinguished reflexions have frequently been omitted entirely and, provided that the purpose of the analysis is the location of the positions of atoms other than hydrogen, there seems to be no objection to this practice when a large number of observed intensities is available.

The problem of obtaining accurate intensities is a very pressing one, since these must be available if x-ray crystallography is to compete with spectroscopy in the determination of accurate molecular parameters. If the

object of an x-ray determination is merely the solution of a stereochemical problem, the intensities can be very crude. If bond lengths reliable to about  $\pm 0.02$  Å are required, then careful, three-dimensional, photographic intensities are usually sufficient. If, however, bond lengths are needed to the third decimal place, and particularly if it is hoped to obtain a detailed picture of the electron distribution within a molecule, all the intensities will need to be obtained with counters, and a reliable correction for extinction will need to be applied. Much work is being done to improve the speed and accuracy of intensity determinations, and most of the major problems have been solved. However, a really accurate x-ray structural determination is still awaited.

Suppose that a set of intensities of 100 per cent accuracy were available. Then it is by no means a simple matter, even after the phase problem has been solved, to arrive at the correct electron distribution, and hence the correct molecular parameters. The refinement procedure, which is the third and last major stage in a crystal structure analysis, has received much attention lately, and some notable advances have been made. It was realized very early by Bragg (4) that, if Fourier methods of refinement are used, errors must be present because of series termination. A practical method of correcting this source of error was proposed by Booth (5), and all x-ray determinations which make any claim to accuracy must include such a correction. If least-squares methods of refinement (6) are used, or if difference syntheses (7) are employed, the correction is made automatically. Since the introduction of least-squares methods of refinement there has been much discussion of the correct weighting factors to use, but this difficulty would largely disappear if the intensities as determined were 100 per cent accurate.

When attempts are made to make the calculated agree with the observed intensities there are basically only two sorts of variables. The first is the atomic coordinates and the second is the atomic scattering factors. At first sight it seems quite clear as to what is meant by an atomic coordinate, but in fact it is not. X-rays determine a time-averaged centre of gravity of the electron cloud surrounding a nucleus, and this is not necessarily coincident with the nucleus itself. It is not known how closely these two quantities agree, but there are reasons for believing that the difference is less than 0.01 Å, except when hydrogen atoms are involved. In the latter case x-rays always seem to find that bonds to hydrogen atoms are shorter than the same distance found by other methods (8). When molecular parameters determined by different methods are compared it is well to remember that different quantities are being measured.

The best values to use for the atomic scattering factors have received much attention lately. For many years the curves of James & Brindley (9) have been used. These have been superseded by curves calculated by McWeeny (10) and then by the curves of Hoerni & Ibers (11) and Berghuis *et al.* (12). There seems to be reason for believing that the McWeeny curve for the carbon atom is perhaps more reliable than the later curves, since the later

workers used the wave function attributable to Jucys (13), and some doubt has been cast on its validity (14).

Since the atoms in a crystal are not at rest it is necessary to modify the calculated scattering factors. This is normally done by means of an empirical temperature factor (15). Much recent work has been devoted to the selection and interpretation of these temperature factors. The determination of anisotropic temperature factors by least-squares refinement has been described by Davies & Blum (16), and Fourier refinement has been discussed by Cruickshank (17). A method by which the individual atomic temperature factors can be used to obtain the translational and rotational vibration tensors of a rigid molecule has been given by Cruickshank (18). Rollett & Davies (19) and Trueblood (20) have listed the effects of crystallographic symmetry on the individual temperature factors. A careful study of the effect of temperature on a limited number of reflexions from a crystal of urea has been carried out by Gilbert & Lonsdale (21), and the discussion of the results has been extended by Grenville-Wells (22).

McDonald (23) has calculated the electron distribution in an isolated hydrogen atom as a function of the temperature factor, but his tentative conclusion that the electron distribution in a bonded hydrogen atom is adequately represented by the electron distribution in an isolated atom seems to be contrary to the experience of most workers. It is usually accepted that the more electronegative the atom to which the hydrogen is attached, the more difficult it is to find the hydrogen atom, and when the hydrogen atom is involved in hydrogen-bonding it becomes very difficult indeed to find by means of x-rays. Thus, for example, Ayerst & Duke (24) could not locate the hydrogen atoms in oxamide despite the simplicity of the structure. However, it is important to notice that McDonald compared his theoretical results with structures for which the intensities had been obtained with great care, and the difficulties that most workers experience may merely be another illustration of the need for accurate determination of intensities. McDonald (23) points out that hydrogen atoms taking part in strong hydrogen-bonding show some unusual features, and this alone suggests that the problem is not finally settled.

There has been a number of papers dealing with the interpretation of anisotropic temperature factors. Blackman (25) has pointed out that information about the vibrational spectrum of a crystal can be obtained from the effect of temperature on the Bragg reflexions. Authier (26) has utilized this effect to decide between two possible frequency distributions for a crystal of zinc blende. Cruickshank (27) has shown how the values obtained for the amplitudes of angular oscillation of the anthracene molecule may be correlated with the low-lying lattice vibrational frequencies which are normally obtained from the Raman spectra of crystals. A knowledge of the values of these lattice frequencies is essential for the calculation of the thermodynamic properties of crystals, and the fact that there is now an independent method of obtaining and checking lattice frequencies is of great

value. It is important to remember that, at the moment, empirical temperature factors must be used with caution. Any systematic errors that are a function of the Bragg angle will be included in the temperature factors, and the absolute values of the temperature factors may be far removed from those obtained from photographic intensities. Relative values of the anisotropic thermal factors will no doubt be much more reliable, but once again the importance of collecting accurate intensities is apparent. There seems to be every indication that the way is now open for some interesting developments in the understanding of lattice vibrations and perhaps, as a consequence, in the theory of melting.

Suppose now that a set of intensities of 100 per cent accuracy were available. Suppose that a model which reproduced these intensities exactly had been selected. Suppose further that a bond length could be defined as the distance between the corresponding time-averaged maxima in the electron density. Even so an x-ray analysis may not yield the correct atomic positions. There may still be an error in the bond lengths. This source of error was discovered when the results of a careful x-ray analysis of benzene by Cox, Cruickshank & Smith (28) were compared with those obtained by Stoicheff (29) from an analysis of the rotational Raman lines of  $C_6H_6$  and  $C_6D_6$ . The C—C bond length obtained by means of x-rays was significantly shorter than that obtained spectroscopically. In order to make quite sure that there were no errors in the Raman work, Langseth & Stoicheff (30) confirmed the original results by analyzing the rotational spectrum of  $C_6H_3D_3$ . The source of the discrepancy was discovered by Cruickshank (31), and shown to arise from the thermal motion of the molecule in the crystal.

If an atom is moving along the arc of a circle, the apparent position of the atom will be displaced towards the centre of the circle. This can be seen in a naive way from Figure 1 which is taken from Cruickshank's paper.  $P$  is the rest position of the atom which is making rotational oscillations with  $O$  as centre. Suppose that the atom spends half its time at  $Q$  and half at  $Q'$ .

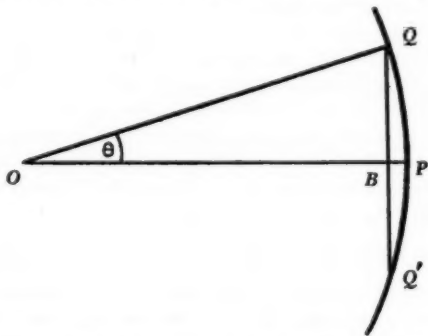


FIG. 1. Peak displacements in angular oscillations.

Then the time-averaged electron density will have its maximum at  $B$ , and the atom is displaced from its rest position by an amount

$$BP = r(1 - \cos \theta) = \frac{1}{2}r\theta^2, \text{ for small values of } \theta.$$

In benzene it was found that  $\theta = 8^\circ$  and  $r = 1.39 \text{ \AA}$ . The error is then  $0.014 \text{ \AA}$ . The more detailed treatment by Cruickshank (31) shows that this figure is of the correct order of magnitude, and the x-ray value for the C—C bond length in benzene, obtained at  $-3^\circ\text{C}$ ., needs to be increased by about  $0.015 \text{ \AA}$ , which brings the value of the length into agreement with that obtained by Stoeicheff.

In principle, this correction needs to be applied to all crystal structure analyses: in fact there are reasons for believing that it will be negligibly small for many. It is likely to be most important for small planar molecules and there is no doubt, for instance, that the C—N bond length in *s*-triazine given by Wheatley (32) is about  $0.02 \text{ \AA}$  too short. This has again been shown by an analysis of the rotational Raman spectra of normal and deuterated *s*-triazine (33).

It is important to notice that the correction required for oscillation about a twofold axis of benzene is as important as about the sixfold axis. This leads to a difficulty in benzene and in similar monocyclic molecules such as the azines. The motion of the atoms normal to the plane of the molecule is compounded of two parts: (a) the translational motion of the molecule as a whole, and (b) oscillation about axes in the plane of the molecule. There are insufficient thermal parameters determinable by x-rays in these unsubstituted monocyclic molecules to decide how much of the motion normal to the plane is translational and how much is oscillational. This results from the fact that x-rays cannot yet determine the anisotropic thermal parameters of the hydrogen atoms. Thus it is impossible to find the total correction needed to be added to the bond lengths. For this reason it is not only advantageous but it is imperative to work at low temperatures if accurate bond lengths are required for molecules of this type.

The refinement of anthracene carried out by Cruickshank (27) has allowed for the effects of thermal motion, and is without doubt a landmark in the determination of molecular structure by means of x-rays. However, the analysis suffers from the fact that the intensities used were obtained photographically and, although they were obtained with great care (34), they are not of the accuracy that can be obtained with counters. When a similarly detailed refinement is carried out with 100 per cent accurate intensities, the results should be very interesting indeed.

#### THE STRUCTURES OF SOME ABNORMAL MOLECULES

The resolution of the initial discrepancy in the dimensions of the benzene molecule has emphasized again the fact that there are very few examples in which a molecule definitely has different dimensions in different circumstances. Furthermore, such a wide variety of molecular structures has now

been investigated that it is possible, with occasional aid from the theoretical chemists, to predict the configurations of many molecules whose structures have not yet been experimentally verified. Nevertheless, a number of cases occur each year in which a molecule is found to have a configuration different from that expected. Such molecules will be termed abnormal for the purpose of this review, although naturally the definition is rather vague. The great importance of these abnormal molecules is that not only do they direct attention at the fundamentals of valency theory but they should serve as a basis for a greater understanding of the forces within and between molecules. When it is remembered that it is still not known why the inert gases crystallize in the face-centred cubic rather than the close-packed hexagonal structure despite a consideration by Ayres & Tredgold (35) of higher order forces, then it will be appreciated how much there is to learn about forces in crystals. Thus these abnormal molecules provide a fertile field for further experimental and theoretical work.

It is convenient to consider two sorts of abnormalities. The first may be called "microscopic" in which the departure from the expected structure is slight and can be detected only by a careful consideration of the limits of error in the experimental determinations. The second may be called "macroscopic" in which it is clear at a glance that a large-scale deviation from the expected structure is present. Here again the definition of the two sorts of abnormalities is not precise, and there can be no rigid distinction between them.

It is doubtful whether there are any examples of microscopic abnormalities in bond lengths. There are two reasons for this. Firstly, the errors in experiments involving diffraction are larger than in spectroscopic methods, and it is only recently that statistical methods of analysis, such as that developed by Cruickshank (36), have given any confidence in the limits of error quoted. Secondly, the approximations necessitated by the complexity of *a priori* calculations of molecular dimensions are such that only in a very restricted class of compounds can the results be deemed as accurate as experimental values. Thus, even though there do seem to be discrepancies in bond lengths, such as those found in hexamethylenetetramine (37) and pentaborane (38, 39), they cannot really be separated from the experimental errors.

Comparison of experimental and calculated bond lengths is even more frustrating. Calculated bond lengths in heteroatomic molecules are subject to rather large errors and, although discrepancies do appear between such calculated values and experimentally determined quantities, little faith can be placed in their reality. Even in homocyclic molecules such as anthracene and naphthalene, the calculations of Pritchard & Sumner (40) show that the nature of the approximations makes considerable differences in the calculated bond lengths, and comparison with observed bond lengths (27, 41) leads to no definite conclusions.

There seem to be more examples of microscopic abnormalities resulting

from the bending of bonds. This is not unexpected when it is recalled that the magnitudes of bending force constants are so much lower than those of stretching force constants. Indeed what is surprising is that there are not more examples of molecules being distorted by lattice forces. It is quite remarkable how frequently a molecule which is undoubtedly planar in isolation is found to be planar within experimental limits in the crystal. However, the refinement of anthracene (27) seems to show definite buckling of the molecule, and the careful analysis of acridine III by Phillips (42) also indicates deviations from planarity. In cycloserine hydrochloride, investigated by Turley & Pepinsky (43), there seem to be indications that the molecule is not quite planar, since the oxygen atom lies at a distance of 0.06 Å from a plane passing through four of the other atoms. Deviations from planarity are also suggested in the analysis of 4,5-diamino-2-chloropyrimidine by White & Clews (44), and in the investigation of 2,4-diketo-5,6-dihydroxypyrimidine by Alexander & Pitman (45).

There can be no doubt that microscopic abnormalities in bond lengths are always present, since the additional lattice forces operating in the crystal must affect the forces between bonded atoms in the isolated molecule. Similarly, the shapes of all molecules must be altered in the solid phase unless the symmetry of the surroundings is such as to maintain their isolated configurations. The lack of unequivocal evidence pointing to such abnormalities suggests, however, that the distortions are generally quite small.

There appear to be more examples of macroscopic abnormalities. Probably the most interesting and perhaps the most fundamental of these is exhibited by the triiodide ion. This ion was first investigated in 1935 by Mooney who determined the crystal structure of ammonium triiodide (46). The results showed that the two I—I distances were different, having values of 2.82 and 3.10 Å, and that the molecule was not quite linear, the angle being 177°. Since this was early in the days of x-ray crystallography, and since all contributions from the ammonium ion were neglected, it is perhaps not surprising that many people, including Mooney, were prepared to ascribe the departure from  $D_{\infty h}$  symmetry as attributable to experimental error. However a careful analysis of caesium triiodide by Tasman & Boswijk (47) has confirmed the previous results, the two distances being 2.830 and 3.035 Å with a standard deviation of 0.015 Å, and the angle being 176.3° with a standard deviation of 0.5°. Confirmation of the odd behaviour of iodine is found in the structures of caesium tetraiodide (48), tetraethylammonium heptaoidide (49) and tetramethylammonium enneaioidide (50). A theoretical explanation of the departure from the expected symmetrical form of the triiodide ion has not yet been given.

Superficially, the azide ion is similar to the triiodide ion, but there is no doubt that the ion has  $D_{\infty h}$  symmetry in ionic azides such as strontium azide (51). Similarly there is no doubt that the two N—N distances are unequal in covalent azides such as methyl azide (52) or hydrazoic acid (53). On the other hand, there are some metallic azides which may be intermediate be-



tween these two extremes (54). Azaroff (55) has investigated the structures of the two forms of lead azide and presents both infrared and crystallographic evidence for believing that the azide groups are asymmetric. However, he was unable to locate the positions of the nitrogen atoms in the presence of the heavy lead atom so that his conclusions cannot be considered as certain and the dimensions of the azide group in lead azide remain unknown.

Another series of triatomic molecules which present macroscopic abnormalities is the cyanogen halides. The chloride, bromide, and iodide have all been investigated in both the gaseous and solid states. The dimensions of the molecules, all of which are linear, have been determined accurately in the gas phase by means of microwaves. In the solid state all three substances form infinite linear chains with the molecules lying head-to-tail. The distance from one molecule to the next in the chain is given directly by the corresponding cell dimension and hence can be determined very accurately. In each case this distance is much shorter than expected, suggesting strong intermolecular attraction along the chains. The relevant figures are given in Table II, which is taken from the paper by Heiart & Carpenter (56). The bond lengths in the solid state have been determined only for the chloride and show, apart from the short contact distance between the nitrogen and chlorine atoms in adjacent molecules, that the C—Cl bond length is about 0.06 Å shorter in the solid than in the gas phase. An explanation of the observed distances in terms of resonance hybrids involving charge separation is given by Heiart & Carpenter. An equally plausible qualitative explanation is that

TABLE II  
REPORTED BOND LENGTHS IN THE CYANOGEN HALIDES\*

Halide	State	$r(C-X)$	$r(C-N)$	Compression†	Method	Reference
I	Gas	1.995	(1.158)	0.8	MW	(57)
	Gas	1.995	1.159		MW	(58)
	Solid	—	—		XRD	(59)
Br	Gas	1.79	1.13	0.6	ED	(60)
	Gas	1.790	1.158		MW	(57)
	Gas	1.789	1.160		MW	(58)
	Solid	—	—		XRD	(61)
Cl	Gas	1.67	1.13	0.4	ED	(60)
	Gas	1.629	1.163		MW	(57)
	Gas	1.630	1.163		MW	(58)
	Solid	1.57	1.16		XRD	(56)

\* All distances in Å.

† Compression = sum of the bond lengths and the van der Waals radii of N and X minus the relevant repeat distance in the crystal.

the halogen atom is  $sp$  hybridized in the solid state with a consequential shortening of the C—X distance and the formation of a partial covalent bond between the halogen atom in one molecule and the nitrogen atom in the next. The strength of the partial bond seems to increase in passing from the chloride to the iodide, and it would be useful to have the gaps in Table II filled so that the effect on the C—X bond length could be seen.

Another simple ion that has received attention lately is the chlorate ion, which has long been thought to be pyramidal with  $C_{3v}$  symmetry. However, Ricchiccioli (62), in an infrared investigation of 15 inorganic chlorates, finds that the doubly-degenerate stretching vibration is invariably split into two closely spaced lines, and that the doubly-degenerate bending vibration is split in 12 of the 15 cases. In order to explain this, Ricchiccioli makes the interesting suggestion that the chlorine atom is lying slightly off the expected threefold axis. Four of these 15 chlorates have been examined by means of x-rays. In the sodium salt (63) the space-group symmetry of the chlorate ion is  $C_3$ ; in the potassium salt (64) and in the silver salt (65) it is  $C_2$ ; while, in the barium salt, the ion has no crystallographic symmetry (66). In no case is there a significant departure from  $C_{3v}$  symmetry, and the fact that the ion can possess these different crystallographic symmetries in the solid state does suggest that the high  $C_{3v}$  symmetry is indeed correct. It is true, of course, that x-ray crystallography, and in fact any experimental method, cannot specify that the symmetry of a particular molecule or ion is exact. There always remains the possibility of small, undetected departures from exact symmetry. In the present case it is difficult to assess how far the chlorine atom must lie from the threefold axis in order to produce the observed splitting, but chlorine is a fairly heavy atom and small departures from the space-group symmetry should be detected quite easily by means of x-rays, unless the structures contain a statistical distribution of less symmetrical ions.

An explanation of the splitting is certainly needed, but further evidence will probably be required before the idea of a symmetrical chlorate ion is universally abandoned.

A recent infrared study of ethylene carbonate (Fig. 2) by Angell (67) raises some interesting questions. A previous x-ray study by Brown (68) showed that the space-group symmetry is  $C_2$  and that the line joining the two linked carbon atoms makes an angle of  $20^\circ$  with the plane of the carbonate group. Angell presents evidence for believing that the ring becomes planar if the substance is in the vapour or liquid states, or if it is dissolved in carbon disulphide, carbon tetrachloride, chloroform, benzene, or water. A change of this magnitude is unusual. There are, of course, examples such as phosphorus pentachloride and pentabromide, and nitrogen pentoxide where the species are different in the solid and gaseous phases, but for a molecule to maintain the same general geometrical configuration of the nuclei and yet allow angles to bend by as much as  $20^\circ$  is very rare. The similar molecule ethylene thiourea (69) is planar in the solid state, whereas molecules such as 1,4-dithi-

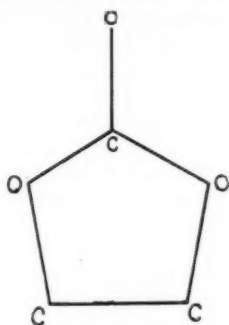


FIG. 2. Ethylene carbonate.

adiene (70), 1,4-dithiane (71), and thianthrene (72, 73) are undoubtedly nonplanar. There is much published experimental and theoretical information about saturated and unsaturated heterocyclic molecules containing nitrogen, sulphur, and oxygen. The picture seems to be rather confused, but some general tendencies can be discerned. Molecules containing nitrogen tend to be planar, as pointed out by Cox & Jeffrey (74). Molecules containing sulphur tend to be bent. If the heterocyclic molecules contain oxygen anything can happen. 1,4-dioxane (75) and 1,4-dithiane (71) are both bent; thiophene (76) and furan (77) are both planar; 1,4-dioxadiene (77) is planar, whereas 1,4-dithiadiene (70) is bent. Finally, ethylene carbonate can apparently be either bent or planar depending on the state of aggregation.

The strange behaviour of oxygen is emphasized in a note by Barclay *et al.* (78) dealing with the pyro-ions. Pyro-ions are generally bent at the central oxygen atom. However, the pyrophosphate ion in zirconium pyrophosphate and in the isomorphous titanium, tin, hafnium, and uranium salts (79, 80) seems to be linear. The space-group symmetry of the ion seems definitely to be established as  $C_{3i}$ . Again a statistical distribution of bent ions may be present in the crystals, but it seems improbable, and it will certainly be extremely difficult to confirm or deny. The pyrosilicate ion is undoubtedly bent in all the compounds so far investigated, including thortveitite and hemimorphite (81). In contrast, however, a recent study by Lord *et al.* (82) of disilyl ether, based on an interpretation of the Raman and infrared spectra of the parent compound and the fully deuterated analogue, leads to the conclusion that the molecule has  $C_{3i}$  symmetry, and hence is similar to the pyrophosphate ion.

There is no doubt that a thorough investigation of the distribution of the valencies about the oxygen atom is warranted and that such a study would probably prove very rewarding.

The abnormality of the remainder of the molecules to be considered could be broadly described as involving rotation around single bonds. Much

of the work on internal rotation has been described by Mizushima (83) and a later review by Mizushima & Shimanouchi (84) includes more recent work. In simple molecules such as symmetrical dichloroethane the position is reasonably clear. The structure with lowest potential energy is the *trans* form, and in the crystal Milberg & Lipscomb (85) have shown that only *trans* molecules are found. The barrier to rotation is small, however, and various physical measurements (83) show that both *trans* and *gauche* molecules are present in the vapour, the proportion being dependent on temperature.

Nevertheless, various pieces of evidence show that the situation is not always so simple. If the vapour or liquid is cooled suddenly, the molecules may not have chance to adopt the most stable form, and Hashimoto *et al.* (86) have shown that symmetrical tetrabromoethane may exist in the *gauche* form in the solid, although Kagarise (87) previously concluded that his solid consisted of the expected *trans* molecules. The dithionate ion is similar to ethane and the expected structure is the staggered form with  $D_{3d}$  symmetry. This has been confirmed in  $\text{NaK}_5\text{Cl}_2(\text{S}_2\text{O}_6)_2$  and  $\text{NaK}_2\text{Cl}(\text{S}_2\text{O}_6)$ . Stanley (88) found the dithionate ion to have crystallographic symmetry  $C_{2h}$  and  $C_i$  respectively, and in both salts the ion has the full expected  $D_{3d}$  symmetry within experimental limits. Similarly in sodium dithionate dihydrate Martinez *et al.* (89) find an ion with  $D_{3d}$  symmetry and  $C_i$  crystallographic symmetry. However, in potassium dithionate Stanley (90) shows the existence of two types of dithionate ion in the same crystal, and neither type has the full symmetry. The two types have crystallographic symmetry  $C_3$  and  $D_3$ ; in the latter, the projected angle between the terminal oxygen atoms is  $23.5^\circ$ , and in the former, the angle is  $54.5^\circ$ , whereas an angle of  $60^\circ$  is required for the full symmetry. Apart from the rotation round the S—S bond, the angles and lengths agree well with previous determinations. The abnormality is no doubt attributable to lattice forces, but it is uncommon to find two such distortions at the same time.

Another set of molecules showing internal rotation involves abnormalities which cannot be ascribed solely to lattice forces. They involve rotation about a bond that is, at first sight, not a single bond and can be typified by the oxalate ion. This ion is planar in every oxalate so far examined with the exception of ammonium oxalate hemihydrate in which the ion is twisted with a dihedral angle of  $28^\circ$  (91, 92). The isoelectronic molecule dinitrogen tetroxide has been shown to be planar in the solid state (93), whereas the infrared spectrum of diborane tetrachloride has been interpreted in terms of a molecule of  $D_{3d}$  symmetry (94). A more recent x-ray analysis has, however, shown that the molecule is planar in the crystal (95). Dipyriddy has been shown to be planar with the molecules in the *trans* form (96, 97). If, however, the ferrous complex of dipyriddy contains a five-membered ring consisting of two carbon, two nitrogen and one iron atom, then rotation about the central bond to form the *cis* molecule must occur. Diphenyl is planar in the solid state (98) but an electron diffraction study indicates that the molecule is twisted in the vapour (99, 100).

In all these molecules a shortened central bond would, on the resonance hypothesis, be expected. In fact in no case does the experimental evidence show such a shortening. There may be traces of a microscopic abnormality, but there is nothing definite. It is clear that an adequate understanding of the structure of these molecules is lacking. On the one hand, it is possible to state that resonance would lead to a planar molecule, in which case the long central bond requires an explanation. On the other hand, it has been suggested (101) that an explanation for the length of the bond is forthcoming, in which case the planarity requires an explanation. A possible solution that has been advanced (102) is that resonance does in fact shorten the central bond, but that the shortening is compensated by repulsion between the atoms attached to the central pair. It is difficult to see, however, why repulsion should exactly cancel the shortening due to resonance in so many cases and, moreover, why molecules such as diborane tetrachloride should remain planar when such strong repulsion is operating. These molecules are all iso-electronic in the sense that there are 34 valency electrons associated with the six central atoms. Presumably, then, an explanation of the structure of one of them should go a long way towards accounting for the structures of the rest. They form a class which merits much further experimental and theoretical work.

This review claims no monopoly of interesting molecules. All molecules are interesting, and probably all molecules possess abnormalities of one sort or another. Personal bias has resulted in the lack of specific mention of many papers which have appeared in the last year. I would like to apologise for these omissions. Some of these papers, such as the report on the structure of vitamin B<sub>12</sub> (103), the account of the determination of the absolute configuration of strychnine (104), and the description of the first neutron diffraction investigation of an aromatic compound (105), are of outstanding importance. However, in order to obtain a deeper understanding of the more subtle forces that control the shapes and sizes of molecules it is necessary to seek out and explain unexpected features in simple molecules. In this review a few of these abnormalities have been mentioned. They require a convincing explanation.

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# COMBUSTION AND FLAMES<sup>1</sup>

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## INTRODUCTION

At least 600 papers were published during 1956 which deal with combustion, less than half of which could reasonably be reviewed within the allotted space. Since an arbitrary selection was necessary, the important subject of detonation and shock waves has been omitted entirely; slow oxidation is covered in another review article. In many cases the selection was based on the availability of papers for perusal and is not to be taken as a judgment of merit; the Russian literature is of course poorly covered. A large number of papers deal less with fundamental combustion as such but try to elucidate problems connected with technical applications. We have attempted to recognize this trend in our organization of topics. The 1956 literature includes the Proceedings of the Gas Dynamics Symposium on Aerothermochemistry (1) and the second AGARD Combustion Colloquium (2). We have also reviewed those papers of the Sixth Symposium (International) on Combustion (3) which could be personally attended. Attention is also called to the Bunsen Society meeting in October, 1956 (4) and to three published treatises (5, 6, 7).

## FLAME PROPAGATION

*Burning velocity.*—The study of burning velocities centered mainly on two objectives: (a) the evaluation of pressure exponents; and (b) the measurement of burning velocity,  $S_u$ , in connection with theories of flame propagation. Lewis (8) and Manton & Milliken (9) found that the pressure exponent of  $S_u$  depends on  $S_u$  itself in such a way that slow flames decrease in  $S_u$  with increasing pressure and fast flames increase in  $S_u$  with increasing pressure. The exponent varies from  $-0.35$  to  $+0.25$ . This rule is based on measurements within a spherical bomb between initial pressures of 1.5 and 0.04 atm. Diederichsen & Wolfhard (10) using a burner method found that  $\text{CH}_4$ -air flames decrease in  $S_u$  from 50 cm./sec. at 0.11 atm. to 6 cm./sec. at 40 atm. Stoichiometric  $\text{CH}_4$ - $\text{O}_2$  flames, however, are independent of pressure between 0.05 and 2 atm. This is generally confirmed by Gilbert (3), who found with a burner method between low pressures and 1 atm. that fast burning flames are independent of pressure, but slow flames have a negative exponent. There seem to be systematic differences between burner and bomb methods. Measurements by Strauss & Edse (11) by a burner method suggest that a positive pressure exponent might exist for hot flames

<sup>1</sup> The survey of literature pertaining to this review was completed in December, 1956.

at pressures between 1 and 100 atm., whereas CO-air flames decrease in  $S_u$  between 1 and 93 atm. from 30 to 8 cm./sec. (12). Fine found a positive pressure exponent for H<sub>2</sub>-air mixtures between  $\frac{1}{3}$  and 1 atm. (13). Singer *et al.* (14) investigated the Bunsen-burner method and found that deformation of flow profile, diffusion of ambient atmosphere and uncertainty as to the correct reference outline render the method difficult. However, large enough burners, especially at low pressures, i.e., large Reynolds or Peclet numbers, will overcome most of these difficulties (15). Flames within the spherical bomb seem also to be subject to distortion, i.e., cells; Troshin & Shchelkin (16) found that the flame front of fast flames within a soap bubble becomes irregular and this leads to excessive values of burning velocities.

Clingman & Pease (17) present a modified Bunsen burner method in which only the middle portion of the flame wave is utilized and flames are made large enough so that the burning velocity is constant over a large part of this flame front. Results for methane-N<sub>2</sub>, A and He "airs" give a pressure exponent which favors a diffusional mechanism of flame propagation. Friedman & Cyphers (18) measured the burning velocities of carbon monoxide-air flames in which they vary the H<sub>2</sub>O content, mixture strength and pressure, while keeping the flame temperature constant [see also Sootmaekers & Van Tiggelen (19); Dove *et al.* (4)]. Friedman & Cyphers discuss their burning velocities in terms of free radical mechanisms; see also Walker (20) and Kurz (21). Spalding (22) proposes a new mixing rule to predict  $S_u$  for mixtures of two combustible gases, taking into account the variation of  $S_u$  with flame temperatures, which may be different for the two components, and Martin (23) applies this rule to mixtures of methane and hydrogen burning with air. Van Tiggelen *et al.* also propose a new mixing rule (4).

Cohen (24) investigated the burning velocity of sulfur monochloride with oxygen and found a maximum value of 105 cm./sec. at about 17 per cent S<sub>2</sub>Cl<sub>2</sub>. Smith & Agnew (3) describe measurements with a constant volume bomb using ionization techniques for flame detection. Henderson & Hill (25) discuss the burning velocities of CH<sub>3</sub>Cl flames. Franze & Wagner (26) present a review of the methods of  $S_u$  measurement.

*Ignition and quenching.*—New evidence was obtained by Fay & Lekawa (27) from the ignition of hydrogen-oxygen and hydrogen-air by converging cylindrical shock waves. By taking the quenching distance as the significant dimension of the zone of heat addition, they show a plausible correlation between their minimum ignition energies and those obtained in spark ignition. The excess enthalpy concept continues to provide lively discussion. Lewis & von Elbe (28) restate the requirement of an enthalpy excess and support their views by reference to minimum spark ignition energies; Linnett (29) argues that excess enthalpy is not a necessary condition for flame propagation since systems do exist in which diffusional processes are important. Khitrin (3) attempts a systematic treatment of thermal ignition

theory which is said to describe successfully a wide range of ignition and limiting phenomena.

Spark ignition is discussed by King & Calcote (30) in connection with the effect of initial temperature, and by Wigg (31) and Swett (3) who are concerned with the ignition of flowing gases. Ignition by heated surfaces is treated analytically by Toong (3) and by Chambré (32) and experimentally by Kumagai & Kimura (3). The ignition of a flowing combustible gas by a neighboring stream of hot combustion products has been considered by Khitrin & Goldenberg (3), by Cheng & Kovitz (3) and by Wright & Becker (33); this interaction is then applied to the problem of bluff body flame stabilization. Some shock strengths for ignition of methane mixtures are given by Giltairé (34). A bibliography on ignition and spark ignition systems was issued on November 1, 1956 (35).

From experiments with  $H_2+O_2$  explosions in chilled Pyrex tubes, Everett & Minkoff (36) conclude that quenching is due to surface adsorption of chain-carrying hydrogen atoms, a process which is inhibited by an ice film on the wall as well as by inert gases. Potter & Berlad (3, 37) studied the quenching of helium- and argon-oxygen-propane flames for test of thermal and diffusional quenching equations, the former being favored. Experimental quenching distances are given for a variety of fuels including liquid hydrocarbons; a correlation between quenching distance and its pressure exponent is discussed. Mozer & Sherburne (38) measured the critical radius for flame propagation in numerous spark-ignited hydrocarbon-air mixtures and discuss this quantity in relation to quenching. Brokaw & Gerstein (3) propose formulae which correlate empirically quenching distance, burning velocity, and ignition energies.

*Flame stability.*—A review of flashback, blowoff, and yellow-tipping has been given by Grumer *et al.* (39); theoretical foundations and extensive experimental data are presented. Treatment is given of the effects of some appliance design factors and of ambient temperature, and rules are proposed for predicting the behaviors of binary and multicomponent fuels. Bollinger & Edse (40) report on the effect of burner-tip temperature on flashback of turbulent flames; Maccallum (41) on blowoff from rectangular burners; Kurz (42) on blowoff using binary fuel mixtures including ethylene as one component. Thomas & Wilhelm (3) raise the blowoff limit by introduction of auxiliary gases near the zone of flame attachment. Mitchner & Gross (43) measured blowoff velocities as affected by radioactivity and by corona discharge from the flame holder. Miller & Setzer (3) have studied flashback and blowoff of *n*-butane-nitrogen dioxide flames, and Streng & Grosse (3) describe the stabilization of an ozone to oxygen flame. Putnam & Dennis (44) review the problem of organ-pipe oscillations and present new data referring to a burner with deep ports. Markstein & Schwartz (45) and Markstein (3, 46) have continued the study of cellular flames and of the interactions of flames with flow disturbances, especially shock waves.

**Flammability limits.**—Linnett & Simpson (3) examine the question of whether fundamental flammability limits do exist. Various candidate explanations of limits are outlined, those that relate limits to chemical properties affecting reaction rate, and those which postulate, at the limit, an instability of the combustion wave to perturbations. New information has been contributed by Otásek (47) on the influence of inert gases; by Scott *et al.* (3) on the  $H_2$ —NO— $N_2O$ —air system; by Cohen (24) on sulfur monochloride; and by Cook *et al.* (48) on ozone-oxygen mixtures. Delbourgo & Laffitte (3) report on the two-lobe flammability region for hydrocarbon-air mixtures and confirm spectrographically that the rich lobe is not a cool flame region.

**Self-ignition.**—In contrast to the work of recent years, there is a definite trend toward measurements with higher hydrocarbons, perhaps reflecting an increased satisfaction with the understanding of the simpler reactions. One notable exception is in the work of Baldwin (49) who measured the first limit of the  $H_2$ — $O_2$  explosion in KCl-coated vessels; having previously developed expressions for the surface destruction of chain carriers, he applies this treatment to his data; the agreement between his observed and predicted limits is impressive. Surface effects on the second explosion limit of CO— $O_2$  are discussed by Roth *et al.* (50). An understanding of the hydrofluoric acid pretreatment of pyrex and silica walls is contributed by Cheaney & Walsh (51).

Freling & Dugleux (52) discuss the optimum concentrations for ignition of paraffin hydrocarbons at subatmospheric pressures. As a follow-up of their work on pentane oxidation, Lucquin & Laffitte (3) have determined ignition ranges of pentane-oxygen mixtures. Norrish & Taylor (53) study the oxidation of some aromatic hydrocarbons in a flow system in the regions of slow reaction and of ignition. Their results are compared with similar data for paraffin hydrocarbons. The slow oxidation of benzene is shown to proceed by successive hydroxylations of the ring to the di-hydroxy stage, whereupon the ring breaks. Ignition is thought to proceed from the instability of a phenol precursor, possibly the phenyl radical. Beckers & Levedahl (54) report on the auto-ignition of benzene-air under rapid compression, and on the analysis of products as found in a motored engine. They consider the most difficult step in the reaction to be the initial attack on the aromatic nucleus.

Swarts & Orchin (55) correlate the spontaneous ignition temperatures of eight hydrocarbons with the behaviors of these hydrocarbons toward vapor phase oxidation. In the case of methylcyclohexane, there is a zone of decreasing oxidation with increasing temperature, corresponding to a range of nonignition. This is said to support the validity of separate high and low temperature oxidation mechanisms. Spontaneous ignition temperatures and ignition lags were measured by O'Neal (56) using representative liquid fuels over an ambient pressure range of 1 to 9 atm. Mecklenborg (57) has studied the spontaneous ignition of some low-flammability lubricants.

Hasid *et al.* (58) discuss the heterogeneous catalysis of propane- $N_2O$  and of cyanogen-air ignitions. Pannetier & Guenot (59) have utilized the inhibiting effect of butane to prevent the explosive decomposition of anhydrous hydrazine during its preparation. An excellent review article on thermal ignition has been contributed by Brokaw (60).

*Flame theories.*—The usual theme of recent publications on theory is that all approaches must lead to essentially the same result, that the major remaining question involves the amount of rigor that may be sacrificed for convenience in computation. Thus the most vigorous disagreement at this time concerns the simplifying assumption of steady-state radical concentrations. One distinctly novel approach to burning velocity theory was attempted in 1956, by Eyring *et al.* (61): the flame front is said to propagate by the random walk of chemical energy, at a rate determined by the value of  $n$ , the ratio of collision rate to reaction rate. While the evaluation of  $n$  requires the same detailed knowledge of kinetics and mechanism that constitutes the stumbling block to all flame theories, Eyring's fresh descriptive language will be applauded and the basic concept will surely have influence.

Penner & Crowe (62) have followed the methodology of von Kármán and collaborators to derive a burning velocity expression for hydrocarbon-oxygen-inert mixtures; diffusion is neglected and a second-order rate-controlling step is assumed. Experimental data for lean mixtures were successfully correlated. Spalding (63) presents a general method for flames with a nonbranching chain. This is applied to the hydrazine decomposition flame and gives a correct prediction as to the effect of temperature. Specific objection is raised in this paper to the steady-state assumption. Giddings & Hirschfelder (3) have considered flames supported by chain-branching reactions. They show that when the chain-breaking step is second-order in the radical concentration, both chain-initiating and chain-propagating steps can be ignored, leaving a much simplified scheme for calculation. A criterion is given for the deviation of free radical concentrations from their pseudo steady-state values. Van Tiggelen & Deckers (3) comment on the necessity for considering chain-branching in the development of flame theory.

Sandri (64) presents a general theory which claims to neglect no major influences and which is mathematically more simple than either the exact method of Hirschfelder or the method of von Kármán & Penner. The burning velocity expression is tested with ozone-oxygen and methane-oxygen-inert flame data. Rosen (3) sets up steady-state propagation equations for ozone flames and determines the time-dependent behavior of a small perturbation. Stable solutions are found for high ozone concentrations but not for dilute mixtures. Mayer & Carus (65) employ a much simplified flame model to derive an expression for the heat generation term; the method is claimed to describe qualitative variations of flame thickness and burning velocity as functions of the physical parameters. Gilbert & Altman (3, 66) and Campbell (3) discuss the relationship of Br atom concentration to steady-state value in HBr flames; their conclusions are contradictory.

## STRUCTURE OF FLAMES

*Probing of flames and temperature measurements.*—The trend toward making detailed measurements of the structure of premixed flames is continued. Fristrom follows up his flame zone studies by investigating the application of one-dimensional flame models to three-dimensional flames (67). The gas velocity normal to the flame front is independent of flame shape up to nearly maximum temperature; thus "burning velocity" does not depend on flame shape. Hydrocarbon reactions within the flame can be divided into two sections. The first step leads to CO and H<sub>2</sub>O; this step determines burning velocity. The second step is only loosely coupled with the first and leads to equilibrium.

A study of the reaction zone of CO flames was made by Rozlovskii (68). The study of flames using radioactive tracers is discussed by Kopytoff *et al.* (69). Jost & Krischer (70) analyze the burned gases of fuel-rich polyhedral flames in the ridges and depressions. Their results are consistent with preferential oxygen diffusion into the depressions. Friedman (71) considers critically the results of flame gas analysis as influenced by diffusion; his latest work is discussed briefly in (72). Weinberg (73) having previously shown that the "schlieren image" in a flat flame occurs at a temperature in the flame front close to  $T = (3/2)T_0$  (in °K.) investigates the schlieren position for conical flames and finds  $T \leq (3/2)T_0$ . He also suggests (74) a new reference point on a flame shadowgraph to correlate with the flame front. Weinberg *et al.* (75, 76) suggest using light deflection to measure final flame temperatures. Although this will not be a very accurate method, it might be valuable for the study of the effect of additives on flames. Saunders & Smith (77) use phase contrast photography to detect refractive index changes in flames. This method may supplement schlieren methods because of its high potential sensitivity.

An interesting new tool for the measurement of transient high temperature is described by Rabinowicz *et al.* (78) which may become important for flames as well as shock tubes, for which it was designed. It consists of a metal film of  $10^{-6}$  cm. thickness on an insulator. The response time of this resistance thermometer is 1  $\mu$ sec. Miao *et al.* (79) used the sodium line reversal method to investigate transient temperatures in closed bomb explosions with central ignition. Their results are not in agreement with theoretically derived temperature profiles.

*Turbulent flames.*—A large part of the effort in this field is directed to the "brush" structure of Bunsen burner-type turbulent flames. This old interest has erupted again following Summerfield's postulate of a "zone of reaction distributed in depth" in the brush of a laboratory slot burner flame (80). Proponents of this reaction zone structure, of the wrinkled laminar wave model, and of randomly distributed flamelets or balls of fire were heard in representative discussion at a panel meeting on turbulent flames (81). Further discussion is contributed by Wohl (3). Richardson (82) advances a mathematical theory of turbulent flames based on the wrinkled wave model.



Turbulent burning velocities on Bunsen flames with premixed flow were measured by Richmond *et al.* (3) and by Wagner (83). The former gave special attention to corrections for flame brush curvature and for the divergence of approach gas flow. Burning velocities at high Reynolds numbers are shown to be independent of height in the flame and to vary directly with the intensity of approach flow turbulence. The situation at low Reynolds numbers remains unclarified. Simon & Wagner (84) point out the difficulties in burning velocity measurement and suggest that flame space and space heating rates may be more significant in characterizing turbulent flames.

A number of investigations have been made of the growth rates of free flames initiated by spark in turbulent streams [Mickelsen & Ernstein (3, 85); Olsen & Gayhart (86); Bolz & Burlage (87)]. The common finding is a low propagation rate, apparently less than in stabilized flames, and even less in some cases than was found with laminar free flames. The effect of turbulence was found generally to depend on the equivalence ratio of the combustible. Mickelsen & Ernstein report an influence of turbulent scale, while Olsen & Gayhart find different effects of isotropic and nonisotropic turbulence and conclude that velocity gradients are of prime importance in accelerating propagation. Iida (3) reports an effect of flame (generated) turbulence in a propane-air free flame; negative findings as to flame turbulence in stabilized flames are reported by Westenberg (88) on the basis of helium diffusion; by Gross (89) on the basis of hot wire anemometry; and by Richmond *et al.* (3) from burning velocities and electronic probe data. Jensen (90) points out that open flames and confined flames should differ radically in the velocity gradients which are alleged to set up flame turbulence.

Flames in ducts have been studied from varying points of view. Weiss (91) has observed a flame spreading from a V-gutter baffle and computed equivalent turbulent burning velocities which range from 5 to 50 ft./sec. The pressure exponent depends on burner geometry and varies from 0.1 to 0.7. Ievlev (3) comments on similarities between combustion in a refractory duct and in a free flame and describes the increases of heat release rate obtained by inserts in the gas stream. Blackshear (3) imposed sound waves on a flame anchored within a duct. His heat release rate was increased by as much as 30 per cent by a disturbance of optimum frequency. Zelinski *et al.* (92) determined burning rates of confined flame jets and correlated their results with the parameters of flow and confining geometry. Turbulence-inducing screens upstream of the flameholder had no effect. Albright & Alexander (3, 93) have measured the stability limits of cyclonic flames in ducts. Flames produced were stabilized at "superficial" velocities up to 700 ft./sec. Predvoditelev (3) claims to have compared reaction rates in turbulent flames with theoretical rates by making use of a correction term of hydrodynamic character.

Williams *et al.* (3) have shown that the atomic composition of gases in the immediate wake of a flame holder can be significantly different from that of the approach stream. By withdrawing the boundary layer from the flame

holder, they were able to accentuate this difference in composition and to extend or curtail stability limits in a predictable manner.

*Flame spectroscopy.*—The question of abnormal rotational temperatures of OH in flames seems to be finally settled. Gaydon & Wolfhard (94) interpreted their rotational measurements of low pressure flames by assuming a non-Boltzmann distribution of the emitting OH radicals. This was disputed by Penner (95), who showed that self-absorption and nonuniform temperature distribution within the flame can lead to similar apparent anomalies. The decisive question of how much OH self-absorption was present especially in low-pressure flames was left undecided. Broida & Kostkowski (96) use a single and double path method and find that rotational temperature measurements in the burned gas of  $C_2H_2-O_2$  flames above the reaction zone at 1 atm. are appreciably distorted. However highly diluted flames at 1 atm. and low pressure flames show too little OH absorption to affect measurements. The "nonthermal" behavior of OH emission in the reaction zone of flames is therefore beyond doubt. Kostkowski & Broida (97) developed a method of measuring temperatures by using the absorption of the OH band. They find the best way is to use "line absorption" with a background light source having OH emission of much smaller linewidth than in the flame itself. Accurate results can be obtained with peak absorptions up to 98 per cent. Broida & Carrington (98) measured also the average lifetime of excited OH in flames by a fluorescence method. Nearly every collision leads to quenching. Kiess & Broida (99) analyze the {01} and {12} bands of the CH (4300 Å) system.

Probably the most important spectroscopic discovery in connection with flames is the finding of the  $CH_2$  and  $CD_2$  absorption spectrum near 2150 Å. It was obtained by Herzberg & Shoosmith (100) during flash photolysis of  $Hg(CH_3)_2$ . From the relative intensities of the  $C^{13}C^{12}$ ,  $C^{13}C^{13}$  and  $C^{12}C^{13}$  bands in air flames of  $C^{13}$ -tagged acetylene, Ferguson (101) reports that a randomization has taken place in the transition from  $C_2H_2$  to  $C_2$ . Kishko & Miliyanchuk (102) irradiate a propane flame with the light of a mercury arc and find rotational lines due to  $\Delta J = 2$ , i.e., forbidden lines in the  $C_2$  and CH bands. This presupposes absorption of the arc light by the  $C_2$  and CH molecules, which so far were always considered to be present only in minute concentrations. Rossikhin & Tsykora (103) investigated the spectra of flames produced by high frequency discharges.

Vaerman *et al.* (104) propose that the activation energies for the formation of OH, CH,  $C_2$ , CN and NH can be deduced from emission flame spectra, obtaining values of the order of 30 to 40 kcal. These conclusions might be of great importance for the understanding of processes in flames; however a clearer understanding of the excitation processes would be of prior importance. Knipe & Gordon (105) reinvestigated the spectrum of  $CO-O_2$  flames. They find evidence for the absorption of an excited  $CO(^1\Pi)$  molecule within the emission spectrum of the flame. They postulate that the continuum emitted by the flame involves a reaction of this excited CO; i.e.,



with the emission of continuous light. If these conclusions are correct, they would change considerably the accepted picture of CO combustion. Further evidence will be necessary before their view can be accepted, especially as to how a molecule can absorb within the emitting flame. Barrère (106) studied the intensities of  $\text{C}_2$  and CH bands on an inverted Bunsen burner. He avoids therefore absorption of light from the burned gas. The position of band intensity maxima is measured. Charton & Laffitte (107) measured the intensity ratios of  $\text{C}_2$  bands relative to the 3900 Å CH bands depending on mixture strength. The result indicates interesting intensity changes with mixture strength for the {20} {10}, and {00} bands of  $\text{C}_2$ . Tawde & Laude (3) also measured band intensities in premixed flames.

Gaydon & Moore (108) studied the emission of the cool flames and preignition glow of propane-air and oxygen mixtures. The cool flames show only formaldehyde bands, whereas the preignition glow emits HCO and sometimes strong OH bands with weak CH and CO-flame bands. It therefore resembles the spectrum of a hot flame at least for oxygen rich mixtures. Methane and formaldehyde produced no preignition glow; however, carbon monoxide emitted the CO flame bands. Vanpée (109) in contrast found a luminescence when he reacted formaldehyde with oxygen at 500° C. He believes that this radiation occurs during the decomposition of an intermediate. No spectral observations are available. Neu (110) followed the slow oxidation of butane with and without cool flames directly with an infrared spectrometer. He finds formic acid, acetic acid, CO,  $\text{CO}_2$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_2$  as intermediates or products.

The spectral emission of high pressure flames was investigated by Diederichsen & Wolfhard (111). Whereas fuel-air flames change their total luminosity very little, oxygen flames become intensely bright. Emission of  $\text{C}_2$  and CH bands is suppressed at pressure above 10 atm. in both flames. Continuous gas emission predominates at high pressure and two types of continua can be distinguished, the CO flame continuum and the hydrogen flame continuum. Mechanisms for this light emission are suggested. The radiation of carbon particles at high pressure is also discussed. Berl *et al.* (112) as well as Parker & Wolfhard (113) observed spectra emitted in diborane and pentaborane flames.  $\text{BO}_x$ , BH and  $\text{B}_2\text{O}_3$  bands are emitted as well as the boron atomic lines. Boranes mixed with hydrocarbons exhibit two reaction zones and preferential borane combustion occurs. Porter & Dows (114) observed an emission of violet color when boron was heated to 1000°C.; they suggest as emitter  $\text{B}_2\text{O}_2$ . At 1250°C. the radiation became green due to the emission of the  $\text{B}_2\text{O}_3$  fluctuation bands.

Bulewicz *et al.* (115) investigated the occurrence and intensity of alkali lines in hydrogen flames. They measure the intensity of the sodium D lines and the Li resonance doublet. Lithium undergoes the reaction  $\text{Li} + \text{H}_2\text{O} \rightleftharpoons \text{LiOH} + \text{H}$ , whereas Na does not. It is possible to estimate the concentration of [H]. In a second experiment they observe the in-

tensity of the sodium D line as influenced by the addition of chlorine ( $\text{Na} + \text{HCl} \rightleftharpoons \text{NaCl} + \text{H}$ ). They find in both experiments that  $[\text{H}]$  is much higher than expected in equilibrium, especially for  $\text{N}_2$  diluted flames.  $[\text{H}]$  becomes in fact nearly independent of flame temperature for high  $\text{N}_2$  dilution. Conditions within the reaction zone could not yet be studied.

The work in Cambridge on flash photolysis has been continued. Complications arise due to the fact that the flash-triggered explosion of mixtures is not entirely homogeneous [Thrush (116)]. Detonation waves travel through the vessel and give rise to strong emission peaks. This renders the interpretation of emission spectra in flash photolysis uncertain. Erhard & Norrish (117) photolyzed  $\text{C}_2\text{H}_2\text{—O}_2$ -amyl nitrate mixtures and observed an induction period after which OH radicals appeared in absorption and emission. The introduction of lead tetraethyl extended this induction period and PbO bands could be seen in absorption, but disappeared after the induction period when atomic lead appeared. Erhard & Norrish conclude that PbO is reduced by chemical action and in this course inhibits partially the main oxidation reactions and leads to a slower heat release. The action of lead tetraethyl is therefore considered truly homogeneous. Thrush (118) flash-photolyzed hydrogen azide and found a new absorption spectrum around 2700 Å which he provisionally assigns to  $\text{N}_3$ . Moore *et al.* (119) investigated the spectra emitted from H or O atomic flames with ammonia and hydrazine. Only weak NH and  $\text{NH}_2$  bands could be found in emission in the  $\text{H} + \text{N}_2\text{H}_4$  flame; but OH and NO bands occurred in addition in the  $\text{O} + \text{N}_2\text{H}_4$  flames.

Nelson & Ramsay used a sapphire reaction vessel to allow transmission of short wave ultraviolet light. They were able to detect radicals in absorption so far unobserved in flash photolysis (120).

*Products of combustion and carbon formation.*—The concentration of  $\text{H}_2\text{O}_2$  in product gases is shown by Prot *et al.* (121) to depend on mixture strength. Propane flames show two maxima which correspond with pressure minima if the "low-pressure stability limit" is plotted against vessel dimension. Everett & Minkoff (36, 122) present further experimental details of their explosions in chilled vessels, where they previously found up to 30 per cent  $\text{H}_2\text{O}_2$  on the walls. They now abandon the reaction  $\text{OH} + \text{OH} + \text{wall} \rightarrow \text{H}_2\text{O}_2 + \text{wall}$  because the  $\text{H}_2\text{O}_2$  concentration is independent of the OH concentration in the gas phase. It is assumed instead that the processes leading to  $\text{H}_2\text{O}_2$  on the wall are connected with the afterglow rather than the flame front of the explosion and that part of the  $\text{H}_2\text{O}_2$  is formed in the gas phase. The proposed reaction both at low and high pressure involves  $\text{HO}_2$ . Cullis & Newitt (3) isolate hydrogen peroxide during the slow combustion of alcohols.

Fetting & Wicke (123) obtain a yield of up to 26 per cent  $\text{C}_2\text{H}_2$  from partial combustion of methane at optimum preheat and mixture strength. The combustion gases were chilled in a vortex of nitrogen. Stand (124) also investigated this problem. Crumley & Fletcher (125) measure the  $\text{SO}_3$  formed in the products of flames from  $\text{SO}_2$ , which is itself formed directly

in the flame from sulfur-containing fuels.  $\text{SO}_2$  concentration increases with flame temperature. Weisenberg & Winternitz (3) consider the use of a rocket motor with an expanding nozzle for freezing out products of combustion and applying the principle to the NO synthesis. Luft (126) presents a nomogram which allows calculation of the product composition of rich flames.

The problem of carbon formation in flames is still under active investigation. Cole & Minkoff (127) studied a flat diffusion flame near the carbon zone with an infrared spectrometer. They found the acetylene band at  $13.7\mu$  both in absorption and emission when using ethylene as fuel. Methane-oxygen flames did not give rise to this band; carbon formation is also reduced compared with ethylene. Comerford had previously studied the formation of carbon by pyrolyzing hydrocarbons in a hot gas stream. He now follows up this investigation by studying the decay of carbon particles in the presence of secondary air (128). Air diffusion is found to be rate-controlling. Zaitseva & Tverdokhlebov (129) observed the growth of carbon on the electrodes when an arc was stuck in acetylene and air mixture. This growth was prevented by traces of alkali salts in the arc.

Fenimore *et al.* (3) correlate the onset of carbon formation for a variety of flames with the concentration of methane and acetylene in the burned gas. Benzene flames are exceptional in that soot does not seem to be formed via acetylene. Stehling *et al.* (3) studied carbon formation in thermal reactions of acetylene diluted with inert gas. At  $600^\circ$  only a fog of liquid polymers was obtained, whereas at  $800^\circ$  carbon particles (solid particles) were observed. The influence of additives was investigated. Aten & Greene (130) study the growth of carbon after the passage of a shock wave by measuring the turbidity of the gas. The process can be described as having an activation energy of 29 kcal., a value in good agreement with rate values for the polymerization of acetylene at low temperatures. Sweitzer & Heller (131) studied carbon formation in large flames, as used for the manufacture of carbon black. Their evidence is consistent with the oil droplet theory of carbon formation, i.e., each carbon particle is preceded by a droplet of condensed oily matter. Cabaune (132) reviews experimental and theoretical work up to 1955.

*Diffusion flames.*—Smith & Gordon (133) studied conical diffusion flames by sampling traverses. Their results show a small amount of oxygen penetration into the fuel and an extensive pyrolysis of the hydrocarbon to form  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ , etc. In many diffusion flames the level of  $\text{C}_2\text{H}_2$  found on the fuel side correlates with the amount of soot observed. Benzene flames are, however, a notable exception as very little  $\text{C}_2\text{H}_2$  is found despite its strong sooting. The authors (134) also investigate alcohol flames. They find again pyrolysis of the fuel. Although propyl alcohol flames soot much stronger than ethanol flames, they have nearly the same concentration of benzene and acetylene as intermediates. Formaldehyde is the most important intermediate in the methanol flame. Powell & Browne (3) investigate the dynamic stability of laminar diffusion flames. Flickering is considered as due to shear forces between the two parallel fuel and air streams. They investi-

gate also the position of the flame in relation to the original position of the fuel and air streams, departures from Burke & Schumann's analytical predictions are due to hydrodynamic effects. In a second paper (3) Browne & Powell investigate theoretically and experimentally the composition of original gas and products across a flat diffusion flame at pressures between 0.1 and 1 atm. They find a high degree of similarity in the distribution of the initial fuel and oxidant, unless soot escapes from the flame. Wolfhard investigated the pressure limits of diffusion flames (15). Unlike premixed flames, normal upright diffusion flames cannot be burned to extremely low pressures and "low pressure limits" exist. Diffusion flames, however, can be burned in such a way that the flame has no "base" where heat losses are usually very great (for example, flame burning downwards from a hemispherical porous disc). Such flames become indistinguishable from premixed flames at low pressure.

#### TECHNICAL COMBUSTION

*Rocket combustion.*—The investigation of nitrates and nitrites is of great interest to rocket combustion. These compounds serve as a model for the more complicated propellant burning. Steinberger (135) reviews recent investigations. The mechanism of the methyl nitrite decomposition flame is discussed by Arden & Powling (3) as well as Gray & Pratt (3), the problem being the decomposition of NO at the low temperatures of this flame. The course of the reaction was followed by measuring the gas composition through the reaction zone. First, decomposition into NO,  $H_2CO$  and  $CH_3OH$  takes place followed by partial reduction of NO together with disappearance of  $CH_3OH$  and  $H_2CO$ . Finally, CO and  $H_2O$  are the only major oxidation products. Powling suggests that NO decomposes by forming HNO as an intermediate; Gray & Pratt favor NO reduction by reaction with an alkoxy radical  $CH_3O$ . Hall & Wolfhard (3) compare the spectral emission of methylnitrate, methylnitrite, nitromethane and ethylnitrate burning with oxygen or as pure decomposition flames. It is possible to postulate a qualitative picture of the reactions occurring in the individual zones of these multizone flames from these observations. For example,  $CH_3ONO$  forms a decomposition flame and formaldehyde bands can be observed as a first flame zone.  $CH_3NO_2$  does not emit formaldehyde bands; it also does not form a decomposition flame at 1 atm. although the heat of formation of both substances is nearly the same. Selle (4) studied the propagation of methylnitrite in long tubes.

Flames burning with NO and  $NO_2$  also shed light on the problem of the kinetics of NO. Myerson *et al.* (3) measure self-ignition temperatures for single- and two-stage flames of propane- $NO_2$  mixtures. They analyze the products of combustion after self-ignition and suggest that the single-stage flame involves the formation and decomposition of a direct addition complex formed from propane and  $NO_2$ . The fully developed second stage causes NO to act as oxidizer. Wharton *et al.* (3) study butane- $NO_2$  flames spectro-



scopically. They find that the position of maximum intensity within the second flame zone of CH, CN, NH bands is the same. However, OH has no maximum at all. It is interesting to compare these results with those of Hall & Wolfhard (3) where OH has a maximum and the position of the intensity maxima is not the same for the above mentioned bands. Roth & Rautenberg (136) investigated the self-ignition of  $\text{CS}_2$ -NO mixtures which is about  $800^\circ\text{C}$ . at half an atmosphere. This is a very low value considering the high temperatures normally necessary to initiate for example an  $\text{H}_2$ -NO flame. The  $\text{CS}_2$ -NO explosion emits a strong flash which is mainly a continuum. It is suggested that the reaction  $\text{SO} + \text{N}_2\text{O} \rightarrow \text{SO}_2 + \text{N}_2$  is mainly responsible for the light emission.

The combustion characteristics of diborane have been extensively studied. Roth & Bauer (137) investigated the reactions leading to the second explosion limit at low pressure. McCoy & Bauer (138) measured the heat of formation of the  $\text{BH}_3$  radical. Parker & Wolfhard (113) studied the limits of flame propagation of diborane-air mixtures. The limits are so wide that the limit flame temperatures are only of the order of  $500^\circ\text{C}$ . Mixed diborane-hydrocarbon flames do not follow Le Chatelier's rule. Burning velocities of diborane-air mixtures are very high. Small additions of diborane to hydrocarbons have, however, little influence on burning velocity [Kurz (139)]. Kurz (140) also stabilized diborane-air flames on a vortex burner. He found that under certain conditions the usual bright green flame blew off and a residual blue flame persisted. It would be interesting to see whether the spectrum of this flame is identical with the glow emitted from  $\text{B}_2\text{O}_3$  (114). Combustion with halogens as oxidizer is discussed by Simmons & Wolfhard (4). Gray & Lee (3) measure the dependence of the burning velocity of the decomposition flame of hydrazine on pressure. They find the burning velocity unchanged by pressure, and this suggests an over-all order of reaction of two. The original fission of the  $\text{N}_2\text{H}_4$  molecule cannot therefore be rate-controlling. Hall & Wolfhard (141) come to the same conclusion.

Reckers & Villars (142) investigate the emission and absorption spectrum of the flame above burning double-base solid propellant strands (JPN). Such a flame at high enough pressures has a decomposing surface; above this is a dark zone followed by a luminous flame. They find essentially continuous radiation down to  $3200\text{ \AA}$ , together with atomic lines from elements present in the propellant. It is claimed that  $\text{C}_2$  bands have been observed; it seems, however, that this claim rests on slender evidence as the (OO) band is missing. The absence of  $\text{NO}_2$  absorption in the dark zone is an important observation. The emitted continuum might well be radiation from carbon particles together with continuous gas radiation characteristic of high pressure combustion [compare with (111)]. Sutherland *et al.* (143) investigated the temperature of the flame of ammonium perchlorate solid propellant. They find the temperature to depend on the size of the oxidizer grain and on the ambient pressure. Temperature measurements using the sodium D lines in such a system might easily lead to large experimental errors due to self-absorption



in the cooler layers around the flame. Dickson *et al.* (144) developed an infrared method to determine the composition of the gases leaving the surface of a solid propellant. Only CO and CO<sub>2</sub> could be detected so far. Friedman *et al.* (3) studied the burning of ammonium perchlorate. This monopropellant has the outstanding quality of having not only the usual low-pressure limit of burning, but also an upper limit at 250 atm. This phenomenon cannot yet be explained. Steinberger *et al.* (145) measure burning rates of liquid nitrate esters in pyrex tubes at high pressure. They find the burning rates to depend strongly on whether normal or deuterated compounds are used. From this it is concluded that diffusion of radicals to the surface is an important factor controlling burning rates. Whittaker *et al.* (146) determined the consumption rates of nitropropane-nitric acid mixtures. They studied the influence of pressure on the shape of the liquid surface. Above a certain pressure the liquid surface becomes turbulent. The influence of vessel dimensions was investigated. Only by taking all these influences into account will it be possible to correlate the consumption rate with the more fundamental burning rate. Clemmow & Huffington (147) consider the oscillatory burning of solid propellants and relate it to the temperature distribution within a slab of explosive which is subjected to self-heating. They believe that discrete layers of propellant explode successively, giving rise to the low-frequency phenomenon of "chuffing."

Auble & Heidmann (148) measure temperatures in hydrocarbon-liquid oxygen flames in combustion chambers at 1 atm., using a two-color method. This is based on sufficient carbon being in the flame to make the method applicable. They find temperature variations in phase with acoustical frequencies. Trent (149) inserts a probe into a rocket chamber working at high pressure and determines temperature, pressure, gas velocity, and chemical composition. His detailed results will be mainly characteristic of the type of injector, but it is noteworthy that it is possible to make such measurements under rocket operating conditions. Behrens & Rössler (150) investigated rocket exhaust flames with and without after-burning in the surrounding air. Ignition occurs usually in the center of the exhaust jet behind the shock diamond. Secondary air is entrained directly behind the nozzle and the flame has therefore the appearance of an inverted premixed flame.

Also relevant to rocket combustion are theoretical considerations of Lorell & Wise (151) and Lorell *et al.* (152) who calculate the rate of burning of droplets of a monopropellant fuel such as hydrazine or a bipropellant system. Scholl *et al.* (3) suspect that some combustion instabilities are due to detonations in the rocket chamber. They find that gaseous mixtures of jet fuel and nitric acid support detonation. The question whether detonation in fact will occur in the rocket chamber may be more difficult to prove.

*Ramjet and gas turbines.*—A large number of papers dealing with the more technical aspects of gas turbine and internal engine combustion was read at a joint meeting of the Institution of Mechanical Engineers and the American Society of Mechanical Engineers (153). Problems of scaling of com-

bustion chambers, similarities, low-pressure behavior, etc., were discussed at the AGARD meeting in Liège (2). Flame stabilization behind bluff bodies and nonsteady combustion were discussed at the Gas Dynamics Symposium at Northwestern University (1).

The burning of single and of multiple droplets was investigated by Goldsmith (154), Rex *et al.* (155), and Kanevsky (156). Both pressure and oxygen index of the air influence the burning rate only moderately in agreement with theory. The mass burning rate is proportional to the droplet diameter. The rate constant is influenced by geometry. In practice it seems, however, that an increase in oxygen index has a very large influence on the rate of spray combustion. Kumagai (157) observed the shape and mass rate of burning of droplets in a falling chamber, thus excluding convection. In theory, combustion should cease; however, droplets may be small enough to complete combustion by using up the air in their direct vicinity. Bolt & Boyle (158) burn sprays from a spinning disc and observe single burning droplets. The turbulence in such a spray renders analysis a complex process.

Schaffer & Cambel (159) study the stabilization of a flame in a fast moving fuel-air mixture by blowing a jet of air or oxygen against it. Petrein *et al.* (160) measure combustion efficiency in a duct behind baffles. Baffle size and geometry as well as pressure changes were investigated. Weiss & Longwell (161) correlate the rich and lean blowout limits with the gas velocity divided by can diameter and pressure to the 0.8 power. De Zubay (162) shows theoretically that advantages may be gained by two-stage combustion as compared with a single-stage homogeneous combustion. Hottel *et al.* (3) use two fuels having the same physicochemical properties but different chemical structure in a "stirred reactor." Flow rates for blowout are not the same. It is also shown that such a reactor does not approximate sufficiently the ideal "well stirred reactor" where mixing is instantaneous. Weiss *et al.* (3) measure flame stability in a ramjet burner for fuels of different reactivity. Although over-all reaction rates in an established flame may be an entirely aerodynamic property of mixing, stability depends on chemical factors. Hottel *et al.* (163) study the stabilization of a premixed flame in the boundary layer of a cooled slender rod. This experiment therefore resembled flame stabilization in a Bunsen burner but without the latter's dilution effects. The position of the flame on the rod depends on mixture velocity and mixture strength.

*Internal combustion engines.*—The action of antiknock agents is still under active investigation. Cook & Clouston (164) flash-photolyzed lead tetramethyl and found an absorption band at 3196 Å. Rifkin & Walcutt (165) found the decomposition of tetraethyllead in the "end gas" of an engine to be independent of the fuels and additives tested and of first order with respect to TEL. Ross & Rifkin (166) find that finely divided lead suspended in fuel has no antiknock properties, whereas smoke from a lead arc has. Nebel & Cramer (167) study the ignition of pure carbon and carbon contaminated with lead compounds in heated air. They find a reduction of ignition temper-

ature by about 200°C. This glowing carbon will then preignite the gasoline mixture in the engine. The influence of carbon on cool and second-stage flame ignition is investigated by Lucquin & Laffitte (168). The pressure at which the second stage flame appears is markedly higher, especially at temperatures above 400°C. Terres *et al.* (169) report spatial flame velocities from measurements in a long steel tube. Gasoline subject to knock always shows higher flame velocities than gasoline which does not knock in engines. The spatial flame velocities have a maximum at about 14 atm. and decrease again at higher pressures. The "octane number" is related to these phenomena. Although their conclusions may not be generally accepted, these experiments may be of great potential value. Agnew & Agnew (170) investigate the emission of rich two-stage ether flames. They find the first stage of this cool flame always to emit formaldehyde bands only, whereas the second stage emits only formaldehyde bands for the richest possible mixtures. Slightly less rich mixtures emit in the second stage also HCO and weak CH bands. Agnew *et al.* (3) compare spectra of cool flames from a burner with those in an engine. They find the preflame engine emission to be similar to the emission of the second stage of a very rich cool flame. Firey (3) revives the "detonation" theory of engine knock. In practice it may be difficult to distinguish between a detonation and a very fast self-ignition [compare shock waves occurring in flash photolysis (116)]. Preflame reaction in Diesel engines [Garner *et al.* (171)] shows glows which are measured with a photomultiplier. These glows occur together with the intermediate formation of aldehydes. Meuer (172) describes the new M-Diesel engine, in which the fuel is sprayed against the hot cylinder walls where it slowly vaporizes and then burns smoothly with the air. The combustion chamber walls act as carburetors for the rest of the fuel. Daniel (3) finds that flame quenching at the cylinder walls is responsible for incomplete combustion in the gasoline engine. Five per cent of the fuel is emitted into the air during normal engine running and can then cause smog under unfavorable conditions.

*Furnaces and solid fuels.*—A new series of papers have come forth on performance trials in the Flame Radiation furnace at Ijmuiden. The International Committee reports (173) that coke-oven gas flames can be made appreciably more luminous by replacing 20 per cent of the gas by liquid fuel. Thring (174) suggests from small-scale experiments that the emissivities of gas flames can also be improved either by preheating the fuel or by utilizing a two-stage combustion. Rivière (175) presents general conclusions regarding the radiation of liquid-fuel/coke-oven gas flames as affected by various parameters of operation. Khitrin (3) gives a general review of rate-controlling factors applicable both to burning of a fixed bed and to burning of a suspended dust. Tsukhanova (3) and Koizumi (3) derive equations to represent rate-controlling diffusional processes in a solid fuel bed; the latter claims agreement between prediction and experiment in the burning of activated carbon but not of ash-containing coke. Chukhanov (3) assesses the role of C + CO<sub>2</sub> reaction in coke burning and finds it unimportant below 1500°C. A de-

tailed study of the kinetics of  $C + CO_2$  reaction is reported by Ergun (176). Rossberg & Wicke (177) report kinetic data for burning of pure graphitic carbon.

The burning of suspended dusts is discussed by Yagi & Kunii (3) who developed a cyclone furnace for combustion and gasification; by Ghosh *et al.* (3) who studied the stabilities of pulverized coal flames; by Hattori (3) who measured burning velocities in pulverized coal-air mixtures by stabilizing a steady, inverted cone flame front; by Tret'yakov (178) who finds that the rate of combustion of anthracite is nearly independent of pressure in the 1 to 7 atm. range. Cassel *et al.* (3) report on burner flames of graphite-oxygen and aluminum-air mixtures; small Bunsen-type flames burn faster than large ones. Representative ratios of radiative to total heat transfer were calculated as 0.45 for graphite- $O_2$  and 0.25 for aluminum-air.

In connection with the fly-ash problem Brinsmead & Kear (179) have burned cylindrical pellets of carbon containing from 0.25 to 2.54 per cent NaCl. Release of chlorine is found to exceed that of sodium, the effect being accentuated by water in the combustion air.

*Explosion hazards, fire prevention and fire fighting.*—On the general subject of evaluating hazards, the following papers are noteworthy. A presentation by Babic & White (180) of extensive data bearing on the explosive characteristics of aviation gasoline; the calculation by Van Tiggelen (181) of the maximum quantity of air that is safely admissible to a combustible mixture; explosion pressures in a constant volume bomb as reported by Busch (182) for a variety of fuel-air mixtures; demonstration by Thomas (3) that flames can propagate through air foams in fuels that are well below their flash points. Robertson *et al.* (183) have developed a method of classifying materials as to surface flammability.

Qualitative description of fires on liquid surfaces is of interest in developing methods of fire-fighting. Rasbash *et al.* (184) have studied EtOH, gasoline,  $C_6H_6$  and kerosene flames in a vessel of 30 cm. diameter. They estimate that heat transfer to the surface is mainly by radiation except in the case of EtOH fires where conduction is more important. Blinov (185) reports similar studies using liquid surfaces of varying diameter. At small diameters, the process is a laminar diffusion flame; the vapor flow becomes clearly turbulent, and diffusion of oxygen into the flame correspondingly increased, at a surface diameter of 1 meter. Pavlov & Khovanova (186) made heat transfer determinations on free-burning hydrocarbon fractions.

In the suppression of ignitions and the extinguishing of flames by dusts or by vaporizing liquid agents, the consensus is that chain-breaking reactions must be involved. Belles & O'Neal (3) attempt to interpret the action of halogenated vapors by use of a gas phase chain-breaking term in the NACA quenching equation; the amount of extinguishing agent required is inversely proportional to the chain-breaking rate constant. Simmons & Wolfhard (187) find methyl bromide in diffusion flames to be as effective as in a pre-mixed flame if added to the air supply; considerably higher concentrations

are required if the methyl bromide is added to the fuel. The effect on diffusion flame structure, accompanied by increases in carbon formation and in  $C_2$  radiation, is described. Garner *et al.* (3) find burning velocities of premixed flames to be almost linearly affected by added concentrations of halogenated methanes;  $CH_2ClBr$ ,  $CH_2Br$  and  $CH_3I$  are markedly more effective than the chlorinated methanes. When dusts are used as inhibitors, the specific surface area is generally found to be the primary factor in relative efficiencies. Dolan (3) finds the alkali metal salts to be the most effective class of compounds; materials that melt or decompose below  $200^\circ C$ . are generally superior. Bouchet *et al.* (188) find Na salts to be more effective than K salts in finely divided form, but the reverse to be true with granular powders. McCamy *et al.* (3) conclude that radiation shielding by powdered inhibitors may be of importance.

The ignition of firedamp atmospheres by mine explosives has received continued attention. Grant *et al.* (189) show that atmospheric humidity reduces the ignition probability but only as an inert diluent, replacing oxygen. Ahrens (190) discusses the behavior of the detonation wave in "safety" explosives and the use of inert components in explosive formulae. Hanna *et al.* (191) report on ignition hazards associated with compressed-air blasting using a compressor underground; the principal factor involved is the depression of the lean flammability limit of firedamp-air from 5 per cent at atmospheric pressure to about 2.3 per cent at 10,000 p.s.i. Titman (192) and Hartmann (193) discuss frictional ignition. Weichsel (194) states that incendive frictional sparks are more highly probable when the rust on metal surfaces has a high water content. Intelmann (195) and Hartmann *et al.* (196, 197, 198) discuss the sensitivities of coal dusts and the prevention of mine explosions by wet rock dusting.

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# THE PHYSICAL CHEMISTRY OF PROTEINS<sup>1</sup>

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The existence of many proteins as reasonably pure chemical individuals, frequently in crystalline form, is an outstanding challenge to the chemist. There stands before him the possibility of applying the basic principles of physics and chemistry to these substances and of treating some of the problems of the mechanisms of life in molecular terms. It is no wonder that many physical chemists have been attracted to the study of these fascinating substances. The field has become so active that it is not possible to discuss all recent developments in a review such as this. This article will be concerned chiefly with the problem of the conformations of the polypeptide chains in the soluble (or "globular") proteins and with some of the changes that they can undergo.

The smallest polypeptide that is generally considered to be a protein is insulin, which contains only 51 amino acid residues per molecule (mol. wt. 5700). Sanger and co-workers have recently found that the amino acids occur in two chains held together by a pair of disulfide links (82). One of the chains contains 21 residues, and the other contains 30 residues. The molecular weights of all other proteins are considerably larger, and the polypeptide chains are much longer. The molecular weights range from about 15,000 up into the millions. In some proteins several polypeptide chains are linked together through amino acid side chains, but many proteins consist of a single long polypeptide chain. Even when more than one chain is present in the molecule, at least one of these chains always contains at least 100 residues. There is much evidence that the chains are folded according to patterns that are characteristic of each protein and that the specific properties of proteins depend in a very important degree on the conformations of the polypeptide chains. The native conformation may be partially or completely altered by relatively mild treatment, such as heating in water, or exposure to urea, alcohol, detergents, acid, or alkali. Such treatment almost invariably brings about a loss of the characteristic biological properties, as well as large changes in the physical properties (e.g., solubility, viscosity, and optical rotation). The change is commonly referred to as "denaturation."

The potentialities of the Leuchs synthesis of polypeptides were first fully realized after the end of the second world war. It has now become possible to study synthetic polypeptides of varying composition and molecular weight using the methods of polymer chemistry. Important contributions have been

<sup>1</sup> The survey of literature pertaining to this review was completed in January, 1957.

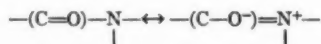
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made to our understanding of the behavior of proteins, and the immediate future promises still more important developments. The appearance of the excellent and comprehensive monograph by Bamford, Elliott & Hanby (11) makes it unnecessary to give a lengthy description of the pertinent developments in this field, but it will be necessary to summarize some of them during the course of this review.

#### THE CONFORMATIONS OF POLYPEPTIDE CHAINS

Normally the detailed structure of a crystalline material may be most completely determined by means of the x-ray diffraction pattern, but protein molecules are so large and complex that it has not yet been possible to carry this procedure through to anything even remotely approximating a complete structure determination for any crystalline globular protein. There is much hope that x-ray crystallographers will eventually develop sufficiently powerful methods to be able to cope with the problem, but it appears that this may require a rather long time. Meanwhile, it is desirable to make use of every possible alternative approach to the determination of protein structures—in fact, the complete x-ray solution will probably be hastened if some reliable preliminary notions of protein structure are available.

One possible approach is to make the very reasonable assumption that proteins are constructed according to the same structural principles as those that apply to other molecules and to try to construct *a priori* models that obey these principles. If not too many models prove to be possible, then this approach ought to be a very useful one. This is, in fact, the method that Pauling and his co-workers have used in trying to understand protein structures. After having examined the crystal structures of many amino acids, simple peptides, amides, and other similar substances related to the proteins, Pauling, Corey & Branson (76) proposed the following set of principles that would be expected to play an important role in determining the ways in which a polypeptide chain may fold. (a) A very important element in the crystal structures of peptides and related substances is the hydrogen bond,  $\text{N}-\text{H}\cdots\text{O}=\text{C}$ , between the amide nitrogen atom on one peptide link and the carbonyl oxygen atom on another peptide group. (b) The six atoms,  $-\text{C}-\text{CO}-\text{NH}-\text{C}-$ , involved in the peptide bond and immediately adjacent to it are invariable coplanar, or very nearly so. This is undoubtedly a result of the strong single bond-double bond resonance that is present in the peptide linkage,



(c) The hydrogen atom involved in the hydrogen bond lies quite close to the line joining the nitrogen and oxygen atoms that are adjacent to it. (d) The bond angles and bond lengths in polypeptides have the same values as those found in simple peptides [see Corey & Pauling (23) for the most probable values]. (e) Disregarding differences in the nature of the side chains, all

amino acid residues in the polypeptide chain must be located in crystallographically equivalent positions. That is, treating all amino acid side chains as identical, the polypeptide chain must be so disposed in space that it is possible to transform one peptide residue in the chain into another by means of simple symmetry operations such as translations and rotations. (Because of the presence of an asymmetric carbon atom in all amino acids except glycine, reflections are not considered, since they transform L-amino acids into D-amino acids.) This principle is based on the observation that whenever crystals are constructed by packing together identical structural elements, all elements tend to have exactly the same surroundings. There is some question whether the principle may be applied to the polypeptide chain folding in proteins, because it disregards the different effects of different side chains on the folding. Unless the assumption is made, however, it is impossible to proceed in any kind of systematic way. Therefore it seems reasonable to accept it as a tentative hypothesis when it is applied to proteins—always remembering that it may not be justified in all cases. In any case it ought to be valid for polypeptides containing a single monomer type. It is important to mention that the amino acid, proline, cannot be crystallographically equivalent to the other naturally occurring amino acids, because the amino nitrogen and  $\alpha$ -carbon atom are present in a five-membered ring; any peptide bond that it forms is subject to special constraints not present in other amino acids. Therefore proline should produce a disrupting effect on the regular folding of polypeptide chains. It has long been known that collagen, which contains an unusually large amount of proline and hydroxyproline, folds in an entirely different manner from other proteins.

In a very general way one can say that the application of these principles will lead to two entirely different classes of polypeptide chain conformations: first, those in which the hydrogen bonding is between peptide links in the same chain ("intrachain bonding"), and second, those in which peptide links in different chains are bonded to each other ("interchain bonding"). Structures that involve mixtures of interchain and intrachain bonding would violate the principle of crystallographic equivalence, but it is conceivable that certain sequences of amino acid side chains in polypeptides might stabilize structures with this mixed type of bonding. For the present this possibility will be disregarded, however.

The structures that are possible with intrachain bonding have been investigated by Pauling, Corey & Branson (76). It is easy to see that for these structures the principle of crystallographic equivalence can be fulfilled for a long polypeptide chain only if it is coiled in the form of a helix having a screw axis of symmetry. (Pauling, Corey & Branson made the important observation that a  $360^\circ$  rotation of the helix need not require an integral number of repetitions of the screw symmetry operations.) It was found that only two kinds of helix are consistent with the five principles listed above. More recently, Low & Baybutt (62) and Donohue (30) have discovered some additional types of helices that are also more or less consistent with these princi-



ples. All of these helices are described in detail by Bamford, Elliott & Hanby (11, p. 119-31) [see also Low & Edsall (63)], and they will not be described here.

Pauling & Corey (72) have found strong evidence for one of these helices—the so-called  $\alpha$ -helix—in the x-ray diffraction patterns obtained from stretched specimens of the  $\alpha$  form of poly-gamma-benzyl-L-glutamic acid (11, p. 263). The x-ray diffraction patterns of  $\alpha$ -poly-gamma-methyl-L-glutamate (11, p. 239),  $\alpha$ -poly-L-alanine (11, p. 257), and  $\alpha$ -poly-epsilon-carbobenzoxy-L-lysine (88) also give strong indications of the existence of the  $\alpha$ -helix as a basic structural element in these materials. The  $\alpha$  form of keratin, the protein of hair, shows x-ray reflections which indicate that the  $\alpha$ -helix is present, although it appears that several helices are coiled together in the manner of strands of a rope [Crick (26, 27); Pauling & Corey (74)]. An x-ray reflection corresponding to a 1.5 Å spacing along the axis of the helix is expected for the  $\alpha$ -helix and not for any other folded configuration of the polypeptide chain that has yet been suggested. X-ray reflections corresponding to this spacing have been observed in  $\alpha$ -keratin by Perutz (78), in the  $\alpha$  forms of many synthetic polypeptides by Perutz (78) and others [Bamford, Elliott & Hanby (11, p. 280)], and in stretched and relaxed muscle [Huxley & Perutz (49)]. According to Perutz, the hemoglobin molecule contains rod-like subunits that may represent helically folded sections of the polypeptide chains; Perutz (78) has observed a weak 1.5 Å reflection along the direction of these rods. Arndt & Riley (6) have found that the x-ray scattering curves from a great many powdered and amorphous proteins resemble the curves expected from an  $\alpha$ -helix more closely than they do the curves expected from any other helical form that has yet been suggested. There is, therefore, very strong evidence that polypeptide chains can in fact fold into  $\alpha$ -helices, and there is also some reason to believe that  $\alpha$ -helices may exist in proteins. With respect to the proteins, however, it must be emphasized that the evidence for the presence of an  $\alpha$ -helix is far from conclusive [see Elliott (36a) and Harker (45)], and that even if the  $\alpha$ -helix is present in proteins it is entirely possible that no more than a portion of the chain is folded in this way. It is interesting that the  $\alpha$ -helix is more nearly consistent with the five Pauling-Corey-Branson principles than any of the other helices that have been described [see Bamford, Elliott & Hanby (11, p. 130)].

Let us now consider polypeptide structures held together by interchain bonds. It is found that many of these structures can be devised which are consistent with the Pauling-Corey-Branson principles. In the so-called  $\beta$  structures the more or less fully extended polypeptide chains are hydrogen bonded to each other through peptide links to form two-dimensional sheets, the sheets being held together by van der Waals forces and other types of bonds. Various  $\beta$ -structures have been described by Huggins (48). Pauling & Corey (73, 75) have suggested several  $\beta$ -structures which they call "pleated sheets," in which the polypeptide chains are arranged in parallel or anti-

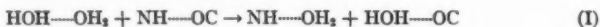
parallel fashion, but with the individual chains crimped so as to conform to the Pauling-Corey-Branson principles. Marsh, Corey & Pauling (65, 66) have given evidence that *Bombyx mori* and *Tussah* silk fibroins have slightly different antiparallel pleated sheet  $\beta$ -structures, and they suggest that  $\beta$ -poly-L-alanine has essentially the same structure as *Tussah* fibroin. Several inter-chain bonded structures have also been suggested which do not belong to the  $\beta$ -family because the polypeptide chains are not hydrogen bonded into sheets. One of these, proposed by Crick & Rich (28), contains polypeptide chains which are rather open helices; this structure is consistent with the x-ray diffraction pattern of polyglycine-II (one of two polymorphic forms that have been prepared for this polypeptide; the other polymorph, polyglycine-I, is believed to be some kind of  $\beta$ -structure). This structure does not contain enough room for any amino acid side chains other than hydrogen atoms, so it is probably unimportant for proteins. A somewhat similar structure has been proposed for poly-L-proline by Cowan & McGavin (24), where the special stereochemical conditions imposed by the five-membered ring of the proline residue and the absence of a hydrogen atom on the imido nitrogen create an unusual situation not encountered in most proteins. A relatively large amount of proline and hydroxyproline is present in collagen, whose structure has recently been elucidated by Rich & Crick (79) and by Cowan, McGavin & North (25). In this structure the polypeptide chains are hydrogen bonded together in groups of three intertwined helices.

In view of the very strong evidence that polypeptide chains actually do fold into an  $\alpha$ -helix in certain synthetic polypeptides, and in view of the indications that the  $\alpha$ -helix may be present in soluble proteins, it has become a widespread practice to use the  $\alpha$ -helix as a basis for interpreting the properties and reactions of proteins. It is well to remember, however, that the evidence for the existence of the  $\alpha$ -helix in globular proteins is still little more than suggestive. We must regard the  $\alpha$ -helix as no more than a very attractive hypothesis. We use it because it is by far the best one available to us, but we must not be surprised if it should turn out that protein molecules are constructed in part or even completely out of structural elements other than the  $\alpha$ -helix. At the very least, however, it is a major advance to have at our disposal this simple and partially substantiated hypothesis as one of the pegs from which we may weave our thoughts about protein molecules and the changes that they may undergo.

#### THE STABILITY OF HELICES

The reasoning used by Pauling, Corey & Branson in deducing the  $\alpha$ -helix puts great stress on the  $\text{N}-\text{H}\cdots\text{O}=\text{C}$  hydrogen bond between peptide units as a factor in stabilizing the helix. In proteins that are dissolved in water, these bonds would be subject to attack by water, which is itself capable of forming strong hydrogen bonds. It is therefore important to consider the inherent stability of the helix in water. Schellman (83, 84) has discussed

this problem in detail. He has first made an estimate of the stability of the  $\text{N}-\text{H}\cdots\text{O}=\text{C}$  hydrogen bond in water through an analysis of the deviations of urea solutions from ideality at different temperatures (83). These deviations indicate a tendency for urea molecules to aggregate, and he ascribes this to the stability of the  $\text{N}-\text{H}\cdots\text{O}=\text{C}$  bond that can be formed between urea molecules. He concludes that the reaction



is endothermic by 1500 cal. per mole. In his second paper (84), Schellman discusses the factors that would be expected to influence the equilibrium



The large number of configurations available to the random coil gives it a large entropy which tends to make this reaction go to the right, whereas the endothermicity of reaction (I) will tend to throw it to the left. Reasonable quantitative estimates of these two effects lead to the conclusion that, in the absence of other factors, the  $\alpha$ -helix and the random coil have almost the same free energy in water at ordinary temperatures, so that relatively slight changes in temperature, solvent, and other factors should have an important influence on the equilibrium. One important factor is the length of the polypeptide chain and the length of the  $\alpha$ -helix that can be formed from it. Because of the "free" hydrogen bonds at the end of an  $\alpha$ -helix (that is, peptide NH and CO groups that cannot be bonded to each other, so that they must be bonded to water), the terminal peptides in the chain have greater freedom of motion than those located within the helix. This has the result that short helices should not be as stable as long ones, and at any temperature there is a minimum length of polypeptide chain that can give a stable helix. Another important factor affecting the stability of helices is the presence of disulfide cross linkages between different parts of the chain because of the incorporation of cystine into the chain. If these linkages are suitably located they will not seriously disrupt the helix (they might, for instance, break it at one point, the two halves being then bent around until they are parallel, with the disulfide link joining the two free ends of the helix). This would decrease the number of configurations available to the random coil and should therefore stabilize the helix. On the other hand, if several disulfide linkages were appropriately introduced into the chain, they could prevent the formation of anything but short sections of helices. Such disulfide linkages might stabilize the random coil form. Interactions between side chains other than cystine would also be expected to affect the stability of the helix. One thinks immediately of the electrostatic attractions and repulsions between side chains bearing charged groups, hydrogen bonds other than those involved in the polypeptide chain itself, and hydrophobic bonds between nonpolar side chains which seek to cluster together in order to escape from the surrounding

aqueous phase. Schellman concludes that "hydrogen bonds, taken by themselves, give a marginal stability to ordered structures, which may be enhanced or disrupted by the interactions of side chains." This conclusion is consistent with the observed great differences that proteins show in the ease with which they may be unfolded (or "denatured"). These differences can evidently result from differences in amino acid composition and in the sequences of the amino acids along the chain. If Schellman's reasoning had led to a particularly stable  $\alpha$ -helix, this would not have been consistent with the variability that proteins show in their resistance to unfolding.

A detailed investigation of Schellman's theory has been made by Peller (77).

#### HELIX-COIL TRANSITIONS IN FIBROUS PROTEINS AND SYNTHETIC POLYPEPTIDES

Twenty-five years ago Astbury & Street (9) and Astbury & Woods (10) showed that the normal x-ray diffraction pattern of the fibrous protein, wool keratin, was transformed into an entirely different pattern when the wool was stretched by about 100 per cent in steam. They concluded that the polypeptide chains in wool are normally folded in some way (now believed to be closely related to the  $\alpha$ -helix) and that on stretching the fibre the polypeptide chains unfold, becoming extended and parallel. They called the two forms  $\alpha$ -keratin (the folded form) and  $\beta$ -keratin (the extended form). Astbury and co-workers later showed that other fibrous proteins could be classified according to their x-ray diffraction patterns into the  $\alpha$  and  $\beta$  types [for a review of this work, see (7)].

In 1949 Ambrose & Hanby (5) noted the similarity of the infrared spectrum and dichroism of an oriented specimen of  $\alpha$ -polygamma-methyl-L-glutamate to the infrared spectra and dichroism of several fibrous  $\alpha$ -proteins. At the same time Bamford, Hanby & Happey (12) found that, depending on the solvent used in preparing the specimen, a polypeptide could give an x-ray diffraction pattern resembling either an  $\alpha$ - or a  $\beta$ -protein. Subsequent work [reviewed by Bamford, Elliott & Hanby (11, p. 302 ff.)] revealed that many polypeptides can be prepared in the solid state in either of the two configurations resembling (though not identical with) the  $\alpha$  and  $\beta$  forms of fibrous proteins. As has already been mentioned, the  $\alpha$  forms of polypeptides are believed to exist in the  $\alpha$ -helical conformation whereas the  $\beta$  forms probably exist as intermolecularly bonded sheets ( $\beta$ -structures). Bamford, Hanby & Happey (13) were able to bring about a partial conversion of some synthetic  $\alpha$ -polypeptides into the  $\beta$  form by stretching in steam. There is thus a rather complete correspondence between the insoluble keratinous proteins and the solid synthetic polypeptides in that each class of substance can exist in two analogous forms which can be converted into each other by mechanical manipulation.

It is of the greatest importance to our understanding of the process of

denaturation in globular proteins that Blout, Doty and co-workers (15 to 18, 31 to 35, 89) have recently been able to demonstrate the reversible inter-conversion of synthetic polypeptides in solution from a helically folded form to a randomly coiled form. Following a careful investigation of the kinetics of the formation of poly- $\gamma$ -benzyl-L-glutamate (PGBLG), this group of workers has been able to synthesize polypeptides of molecular weights up to 800,000 (DP up to about 4000) [Blout *et al.* (17, 18)]. In the strongly hydrogen-bonding solvent, dichloroacetic acid (DCA), these polymers have all of the characteristics of a random coil: the dependence of the intrinsic viscosity on the molecular weight is that of a typical random coil, and the dissymmetry of the light scattering gives a radius of gyration similar to that expected of random coils having similar intrinsic viscosities [Doty *et al.* (31, 32)]. This is what one would expect if DCA ruptures the hydrogen bonds necessary for the maintenance of the helical conformation. When PGBLG of high molecular weight is dissolved in a nonhydrogen bonding solvent such as benzene, chloroform, or ethylene dichloride (EDC), a much more viscous solution is obtained. The reduced viscosities of these solutions are strongly dependent on the concentration of the polymer, indicating a tendency for the molecules to aggregate. The aggregation can be much inhibited (as revealed by a much smaller dependence of the intrinsic viscosity on the concentration) if a small quantity of a hydrogen bond forming substance such as dimethyl formamide is added to the solvent; the intrinsic viscosity of the polypeptide in such solutions varies with the molecular weight in the manner expected of a rigid rod whose length is proportional to the molecular weight, but whose diameter is independent of the molecular weight. The light scattering dissymmetry in such solutions also indicates a rigid rod whose length is proportional to the molecular weight. Both properties indicate that the rods have the dimensions expected of polypeptide chains coiled into  $\alpha$ -helices [Doty *et al.* (31, 32)].

If the molecular weight of the polypeptide is low, the helical form is apparently no longer stable, and instead one finds random coils in all solvents. In solvents having poor ability to form hydrogen bonds, there is a strong tendency to aggregate; the infrared spectrum indicates that the aggregates have structures similar to those found in the solid  $\beta$  form [Doty *et al.* (32)]. The minimum molecular weight that will lead to helical structures in non-hydrogen bonding solvents appear to depend on the solvent and on the temperature.

A transition from rods to random coils can be produced by adding DCA to a solution of PGBLG in EDC [Doty & Yang (35)]. When the DCA concentration reaches 76 volume per cent there is a sharp change in viscosity and flow birefringence, consistent with a transition from a rod to a random coil. The change is reversible and occurs over a relatively narrow range of EDC concentrations. The transition can also be brought about by changing the temperature of a solution containing 76:24 DCA:EDC. It is observed that

the transition occurs over a relatively narrow range of temperatures (about 15°C.). The sharpness of the transition indicates that partially unfolded states of the molecule are not stable. The significance of this is discussed by Peller (77). Very surprisingly, it is observed that in these EDC:DCA mixtures the helical form is stable at high temperatures and the random coil is stable at low temperatures. This is the opposite of what is observed with proteins, where raising the temperature invariably causes the helices to transform into a state resembling a random coil. Doty & Yang ascribe this behavior to the release of a large number of DCA molecules by the random coil when it folds into a helix, the DCA molecules producing a large increase in entropy when they mix with the EDC molecules in the solvent; presumably this entropy of mixing is greater than the decrease in entropy of the polypeptide chain when it is transformed into a helix. This finding emphasizes the importance of Schellman's conclusion that the inherent stability of the helix is not very great and can be modified by relatively slight changes in the environment.

Blout & Idelson (16) have prepared poly-L-glutamic acid (PLGA) by de-esterifying PGBLG with anhydrous hydrogen bromide. This procedure results in practically no change in the length of the polypeptide chain. Oriented solid films of PLGA have infrared spectra and dichroism indicating that the chain is in the  $\alpha$ -helical conformation. If the solid sodium salt of the acid is prepared, the chains transform into the  $\beta$ -configuration. The transformation is reversed when the solid acid is regenerated from the salt. It appears that the electrostatic repulsions between the side chains are responsible for the collapse of the helix. Doty *et al.* (34) have observed helix-coil transitions in solutions of PLGA in water-dioxane mixtures when the pH and temperature were changed.

#### SOME METHODS OF STUDYING CHAIN CONFORMATIONS IN PROTEINS

Having described the  $\alpha$ -helix, the x-ray evidence that supports it, and the factors that affect its stability, let us now consider the effect of the helix on the behavior of proteins. Three properties are especially interesting in this connection because they depend directly on the chain conformation and have been studied in some detail in recent years. These properties are the rate of exchange of hydrogen and deuterium atoms with water, the infrared absorption spectrum, and the optical rotatory power. Many other properties also change when proteins are denatured, but space does not permit a discussion of them here, even though they have also led to interesting and important insights into protein structure.

*Hydrogen-deuterium exchange.*—The ease of the exchange of hydrogen and deuterium atoms between the polypeptide chain and the aqueous solvent is in many ways the most easily interpreted property that should be particularly sensitive to the conformation of the chain. One would expect that the hydrogen atoms involved in the  $N-H\cdots O=C$  bond of a helix



would exchange with the protons of the surrounding water phase (or with the deuterium atoms, if this phase is heavy water) much less easily than would the same atoms in a chain having a random coil configuration, in which the N—H group would be hydrogen bonded directly to the solvent water molecules. Lenormant & Blout (57, 58) first showed by means of changes in the infrared spectrum that some of the hydrogen atoms of the amide groups of serum albumin, gamma globulin, and ovalbumin exchange with heavy water only on heating or on making the solution alkaline. Incomplete conversion of N—H to N—D, as revealed by infrared spectra, has also been observed on exposure to D<sub>2</sub>O of keratin [Parker (71)] insulin, bovine serum albumin, and myoglobin [Haggis (44)] and human hemoglobin [Larson & McLaughlin (55)]. Lenormant (56) finds no slowly exchanging amide hydrogen in soluble silk. A much more quantitative investigation of both the kinetics and extent of the exchange has been made by Linderstrøm-Lang and his co-workers, who follow the exchange by measuring the density of the solvent. This method has the advantage that the actual number of atoms exchanged can be determined very accurately. Lobunez & Karush (61) have described a radioactive counting method that can be used for following the exchange of hydrogen and tritium atoms in proteins. Much of this work has been reviewed by Linderstrøm-Lang (59). Simple peptides were found to exchange all of their nitrogen-bound hydrogen atoms in less than one minute. The same was true of the nitrogen-bound hydrogen atoms in the isolated A-chain of insulin (i.e., the chain containing 21 amino acid residues, prepared by rupturing all of the cystine disulfide cross linkages of insulin with performic acid, followed by separation from the 30 residue B chain). For native insulin, however, it was found that 29 out of 89 potentially exchangeable hydrogens react relatively slowly at pH 3. Furthermore, the 29 protons which exchange slowly do so at widely different rates, indicating that even among the slowly exchanging protons some are much more accessible to the solvent than are others. The exchange is catalysed by alkali [Hvidt & Linderstrøm-Lang (51)] and by the denaturants urea and guanidinium hydrochloride (50, 59). The much greater rate of exchange of the A chain as compared with native insulin indicates that the disulfide cross links must be important in stabilizing the structure that is responsible for the slow exchange in insulin. Whether or not this structure is the  $\alpha$ -helix is, however, not clear. Studies of the optical rotation of insulin by Yang & Doty (89), which will be discussed below, seem to indicate that the disulfide links in insulin interfere with helix formation. Similar indications of the presence of slowly exchanging hydrogen atoms have been obtained with ribonuclease (50) and  $\beta$ -lactoglobulin (51). Recently Berger & Linderstrøm-Lang (14) have found that the hydrogen-deuterium exchange in poly-D,L-alanine also occurs at widely different rates for different atoms along the chain. Presumably there is rapid exchange from residues near the ends and much slower exchange as one approaches the center of the chain. They give reasons for believing that the exchange near the ends occurs by unravelling of the



helix, whereas near the center it must occur at "breaks" which occur when several adjoining  $\text{N}-\text{H}\cdots\text{O}=\text{C}$  hydrogen bonds simultaneously rupture. Surprisingly, urea did not catalyse the exchange in poly-D,L-alanine, raising the disturbing suspicion that hydrogen bonds may not be very important in stabilizing the helix in this molecule. The rate of exchange is dependent on the pH, having a minimum at pH 2.8. Since the chain probably has at most a single positive charge at one end and a single negative charge at the other end, the pH dependence must come from a direct attack of the acid or base on the peptide link, rather than indirectly from unfolding induced by electrostatic repulsions along the chain.

*Infrared absorption spectra.*—Ambrose & Elliott (2) observed that the frequencies of the infrared absorption ascribed to the motions of the  $\text{N}-\text{H}$  and  $\text{C}=\text{O}$  bonds in the peptide linkages of synthetic polypeptides are consistently different in the  $\alpha$  and  $\beta$  forms of the polypeptide chain. These differences are reviewed in detail by Bamford, Elliott & Hanby (11, Chapters VI and VII). Two frequencies are particularly sensitive indicators of transitions between the  $\alpha$  and  $\beta$  forms: These are the  $\text{C}=\text{O}$  stretching frequency and the  $\text{N}-\text{H}$  deformation frequency.<sup>3</sup> A third frequency, that of the  $\text{N}-\text{H}$  stretching mode, is also invariably present, but it is less sensitive to the conformation of the chain. The values that are found for these frequencies in the two forms of the polypeptide chain are given in Table I. All of these fre-

TABLE I  
INFRARED SPECTRA OF POLYPEPTIDES

Nature of Vibration	$\alpha$ form, frequency and dichroism	$\beta$ form, frequency and dichroism	Non H-bonded frequency
$\text{C}=\text{O}$ stretching	1650 to 1660 parallel	1630 perpendicular	1680 to 1700
$\text{N}-\text{H}$ deformation	1540 to 1550 perpendicular	1520 to 1525 parallel	<1520?
$\text{N}-\text{H}$ stretching	3290 to 3300 parallel	3280 to 3300 perpendicular	ca. 8460

quencies for both forms of the polypeptide chain are very different from the frequencies found for  $\text{N}-\text{H}$  and  $\text{C}=\text{O}$  groups that are not hydrogen bonded, as observed for amides in very dilute solutions in nonhydrogen bonding solvents (80). This is a confirmation of the hypothesis of Pauling, Corey & Branson, that hydrogen bonds between peptide groups are important features of the structure of polypeptides.

<sup>3</sup> Fraser & Price (42) have shown that the  $\text{N}-\text{H}$  "deformation" frequency actually corresponds to a normal mode containing a considerable admixture of other motions of the peptide bond beside the bending of the  $\text{N}-\text{H}$  bond.

The dichroism of the C=O and N—H stretching frequencies is another important characteristic useful in distinguishing the two forms of the chain when samples of the polypeptide are available in which the chains have been oriented by stretching or rolling [Ambrose & Hanby (5); Ambrose & Elliott (2)]. In the  $\alpha$  form, the stretching modes of C=O and N—H absorb more strongly when the plane of polarization of the incident radiation is parallel to the direction of stretching or rolling, and the N—H deformation frequency is absorbed more strongly when the plane of polarization is perpendicular to the direction of stretching or rolling. This is just the behavior expected for helices of the type described by Pauling, Corey & Branson, because it would be expected that the axes of the helices would be parallel to the direction of stretching or rolling, and the C=O and N—H bonds in these conformations lie more or less parallel to the axes of the helices. In the  $\beta$  forms of the polypeptides, the dichroic behavior of all three of these bands relative to the direction of rolling or stretching is the opposite of that of the  $\alpha$  form. (See Table I.) This is to be expected if the chains in the  $\beta$ -structure are extended in the direction of stretch, since the C=O and N—H bonds in the  $\beta$ -structures lie more or less normal to the length of the chains.

It is found that when molecules in the  $\alpha$  conformation are dissolved in solvents that do not disrupt the helix (e.g., chloroform and ethylene dichloride), the C=O stretching and N—H deformation frequencies retain the values characteristic of the  $\alpha$  forms in the solid state, regardless of the concentration of the polypeptide [Ambrose & Elliott (2)]. If, however, the polypeptide chains are too short to give stable  $\alpha$ -helices, then the C=O stretching frequency is strongly dependent on the concentration, concentrated solutions giving frequencies close to those characteristic of the  $\beta$  form, and dilute solutions giving frequencies considerably greater than those characteristic of the  $\alpha$  form [Blout & Asadourian (15)]. The abnormally high C=O frequencies in dilute solutions are supposed to be due to a "solvated" form of the group. These findings substantiate the intermolecular nature of the hydrogen bonding in the  $\beta$  forms of polypeptides and the intramolecular nature of the bonding in the  $\alpha$  form.

Blout & Idelson (16) have recently shown by means of the infrared dichroism of oriented films of poly-L-glutamic acid that the free acid exists in the  $\alpha$  form whereas the sodium salt is in the  $\beta$  form. Presumably the electrostatic repulsions between the charged carboxyl groups of the salt make the helix unstable.

Ambrose & Elliott (3) concluded from the infrared frequencies and the dichroism that  $\alpha$ -keratin is in a helical configuration and that  $\beta$ -keratin has a  $\beta$ -structure. The same workers showed that the polypeptide chains in silk fibres are largely, though not entirely, in the  $\beta$  form. It has been known for some time, however, that a water-soluble form of silk may be prepared either by extracting the silk gland of the silkworm, or by treating silk with strong solutions of lithium bromide, or by treating silk with alkaline solutions containing the cupric ethylene diamine complex. Ambrose *et al.* (1) and

Lenormant (56) have shown that this soluble form of silk has a C=O stretching frequency of  $1660\text{ cm}^{-1}$ , indicating that it is not a  $\beta$ -structure and that it may be in an  $\alpha$  form. [Bamford, Elliott & Hanby (11, p. 388) point out that a C=O frequency of around  $1660\text{ cm}^{-1}$  is not by itself conclusive evidence for an  $\alpha$  form of the polypeptide chain, since a similar frequency is observed in polyglycine II and collagen, neither of which contain polypeptide chains in the  $\alpha$  form.] Treatment of water-soluble silk with ethanol or trichloroacetic acid, or stretching a dried film of water-soluble silk, converts it into an insoluble form with a C=O frequency at  $1630\text{ cm}^{-1}$  and a maximum dichroism of the C=O band lying normal to the direction of stretching; these treatments evidently convert soluble silk into a  $\beta$ -structure. The process is a typical example of the denaturation of a protein.

Elliott & Malcolm (38) have studied the infrared spectra of films obtained by evaporating aqueous solutions of soluble silks obtained from four different species of caterpillar. They have also studied films obtained from copolymers containing various proportions of glycine and alanine. The silks vary considerably in amino acid composition but glycine and alanine constitute the major portion of the amino acids present in all of them. The ratio of glycine to other amino acids in the silks varied from 26:74 to 45:55. It was found that in both the silks and the synthetic copolymers, the  $1630\text{ cm}^{-1}$  C=O peak characteristic of the  $\beta$  form tended to be most prominent when the ratio of glycine to the other amino acids was high, and that the  $1660\text{ cm}^{-1}$  peak became more prominent when this ratio was low. The x-ray powder diagram and the infrared spectrum between  $800$  and  $1400\text{ cm}^{-1}$  of the water soluble form of the silk containing the least glycine strongly indicated that it is in an  $\alpha$  form closely resembling  $\alpha$ -poly-L-alanine. Polyglycine itself is known from x-ray work to form intermolecularly bonded structures exclusively, so it is understandable that increasing the proportion of glycine in a polypeptide tends to stabilize the  $\beta$  form relative to the  $\alpha$  form. These results are consistent with Schellman's conclusion that the  $\alpha$ -helix has only marginal stability, and that relatively small changes in the composition of a polypeptide chain can make the  $\alpha$ -helix unstable.

The heat denaturation of globular proteins has also been found to bring about changes in the infrared absorption frequencies that may be explained as by a transition from an  $\alpha$ -helix in the native protein to a  $\beta$ -structure in the precipitated denatured protein. These changes have been most carefully studied by Elliott, Ambrose & Robinson (4, 37) with insulin, but they have also been noted by Ambrose & Elliott (3) on chymotrypsinogen and glyoxalase, and by Chouteau (21) on other proteins. [It should be noted that many years ago Astbury, Dickinson & Bailey (8) showed that the x-ray diffraction patterns from heat denatured protein precipitates resembled those of the  $\beta$  form of keratin.] Uzman & Blout (87) found that the intensity of the N—H stretching frequency in films of pepsin increased by about 40 per cent relative to the C—H stretching frequency when the protein was denatured by exposure to alkaline pH and rapidly returned to pH 4.5, where

the native form is stable. No change in the frequency of the N—H bond was observed to result from this treatment, but it is known that this bond is hardly affected by the  $\alpha$ - $\beta$  transition (see Table I). De Loze & Lenormant (29) report that the protein component of thymus nucleohistone undergoes a transition from the  $\alpha$  form to the  $\beta$  form when it is exposed to the denaturant, xylene sulfonate. The nucleic acid component was unaffected by this treatment. (On the other hand, if the nucleic acid is degraded by exposing it to the action of deoxyribonuclease, no  $\alpha$ - $\beta$  transition is observed in the protein.) It is interesting to mention that Elliott (36) has observed a phenomenon in poly-DL-alanine which is very similar to the heat denaturation of a protein. The  $\alpha$  form of this polypeptide can be produced by evaporating a formic acid solution. This form is soluble in water and it has a CO band at  $1662\text{ cm}^{-1}$ . On heating the solution in boiling water a gel is produced which on drying is found to have an infrared peak at  $1629\text{ cm}^{-1}$  as well as a peak at  $1662\text{ cm}^{-1}$ . Evidently some of the chains (though not all) are converted into the  $\beta$  form by heating, and the interchain cross-linking thereby produced makes the polypeptide insoluble in water. The precipitate still contains substantial amounts of the  $\alpha$  form, however.

The use of infrared with proteins is seriously restricted by the fact that water strongly absorbs in the region of the N—H and C=O frequencies that have just been discussed, so that the protein cannot be present in aqueous solution. This difficulty is rather serious because it is often desirable to study the structure of protein molecules in solution rather than in the dry state. The difficulty can be avoided in part by dissolving the protein in heavy water, which absorbs at much lower frequencies than ordinary water. There are, however, certain advantages in making use of the overtone and combination bands of the C=O and N—H bonds, which lie above  $4000\text{ cm}^{-1}$ , where water is relatively transparent. These bands are also quite weak, so one is not restricted to working with the very thin layers that are necessary with the intense fundamental bands. Work on polypeptides and proteins in this region of the infrared has been reviewed by Bamford, Elliott & Hanby (11, p. 172). The assignments of frequencies in this region to the normal modes of the peptide bond is more difficult than in the fundamental region, because one frequency can represent several normal modes. These assignments have been discussed recently by Hecht & Wood (47).

*Optical rotatory power.*—The optical rotatory power of a substance is known to be extremely sensitive to changes in molecular conformation. Since it is easily measured on molecules in solution, it is well suited to the study of protein denaturation and the changes that occur in the folding of polypeptide chains. Unfortunately, the theory of optical rotatory power as related to molecular structure is still not well understood except in rather general terms, so it is usually not possible to say very much about the nature of the changes in conformation that are responsible for a given observed change in optical rotation. The property, therefore, has to be used as an empirical indication of changes in conformation. Recent theoretical develop-

ments concerning the optical rotations of helices may be important in the study of proteins and polypeptides, however, and will be discussed below.

Although the numerical values of the optical rotations of native proteins vary considerably from one protein to another, all but a very few proteins are levorotatory. (In general  $[\alpha]_D$  lies between  $-20^\circ$  and  $-70^\circ$ .) When proteins are subjected to denaturation conditions that are believed to cause the polypeptide chains to uncoil without precipitating the protein from solution (e.g., exposure to strong urea, acids, or alkali, and heating at a pH not close to the isoelectric point), the optical rotation invariably increases considerably in the levo direction. The amount of the change varies from  $20^\circ$  to over  $70^\circ$ , depending on the denaturation conditions and on the protein. Jirgensons (52), Golub & Pickett (43), and Schellman (85) have recently studied the changes in the optical rotations of a great many proteins when they are denatured in various ways. We shall mention below a few of the many other papers in which optical rotation has been used to study the denaturation of individual proteins.

The fact that all proteins are levorotatory strongly suggests that native proteins possess some common structural element. The tendency for the levorotation to increase on denaturation also indicates that the process involves a structural change that is similar for all proteins. It is natural to suppose that the structural element in question is the  $\alpha$ -helix in the native protein and that the change observed on denaturation in solution is the transformation of this helix into a form more or less resembling a random coil. One is even tempted to ascribe the differences in the optical rotations of native proteins to different degrees of perfection in the helical structure, the fraction of the polypeptide chain that is folded into a regular  $\alpha$ -helix being smaller in a protein with a large levorotation.

These hypothesis have been given substantial support by recent work on synthetic optically active polypeptides. Robinson & Bott (81) synthesized copolymers of gamma-methyl-L-glutamate and DL-phenyl-alanine having varying molecular weights. They observed that in *m*-cresol, a solvent now known to favor the helical conformation (89),  $[\alpha]_D$  varied from  $-18^\circ$  when the degree of polymerization was small to  $+70^\circ$  when the DP was large. Since it is known, as we have seen, that short polypeptide chains do not give stable helices, this is an indication that the change from the helix to a more random coil in a polypeptide containing L amino acids increases the optical rotation in the levo direction.

This agrees with the hypothesis just stated for proteins, which, of course, are also made up exclusively of amino acids having the L configuration. Much more substantial evidence for the hypothesis has recently come from the work of Doty *et al.* (31, 32). As has already been mentioned, the viscosity and light scattering of poly-gamma-benzyl-L-glutamate (PGBLG) reveal that a change from an  $\alpha$  helix to a random coil can be induced by changing the composition of the solvent. It has been found that this change is accompanied by a change in the optical rotation in the levo direction. For in-

stance,  $[\alpha]_D$  for PGBLG is  $+13^\circ$  in chloroform (helical form) and  $-14^\circ$  in dichloroacetic acid (random coil form). Similarly, Blout & Idelson (16) have observed  $[\alpha]_D$  for polyglutamic acid to be  $-8^\circ$  at pH 4.5 (where the infrared dichroism shows that it is in the helical form) and  $-83^\circ$  at pH greater than 7 (where the helix is uncoiled in solution). Doty *et al.* (34) have investigated this change in the rotation of polyglutamic acid in more detail as a function of pH and temperature and have found that it occurs over a relatively narrow temperature and pH range. More recent work by Yang & Doty (89) and by Moffitt & Yang (69) has shown that there are substantial solvent effects on the rotations of both the helical and random coil forms of PGBLG and polyglutamic acid, but the general tendency of the random coil to be more levorotatory than the helix is clearly evident in spite of this.

Some interesting interpretations can be given to changes that have been observed in the rotations of proteins in the light of this work. Native bovine serum albumin has a relatively large specific rotation ( $[\alpha]_D = -61^\circ$ ) possibly indicating a substantial amount of disorganization within the molecule. This disorganization may be a result of the limitations on the folding imposed by the presence of an unusually large number (about 14) of disulfide cross linkages in the molecule (53). When the detergent, sodium lauryl sulfate, is added, the protein becomes even more levorotatory ( $[\alpha]_D = -72^\circ$ ), indicating that the helices may have been even more extensively disrupted. Markus & Karush (64) have found, however, that when the disulfide links are ruptured with  $\beta$ -mercaptoethyl amine in the presence of detergent (no reaction occurs unless detergent is present) the levorotation drops to  $[\alpha]_D = -45^\circ$ . This change is in the expected direction if the rupture of disulfide cross linkages makes possible an increase in the amount of helical folding in the molecule. Similar, though smaller, decreases in levorotation following the rupture of a chemical bond have been found by Neurath, Rupley & Dreyer (70) during the activation of chymotrypsinogen and trypsinogen. The activation process here is known to involve the rupture of the polypeptide chain at well defined loci. It would appear that the folding in chymotrypsinogen and trypsinogen is such that the portion of the chain ruptured on activation may not be able to participate in the helical folding, but that when this section of the chain is severed, the free chain ends are able to coil into helices—perhaps adding onto the ends of helices that are already present in the molecule. Very recently Harrington & Schellman (46) have used optical rotatory power to study the effect of concentrated solutions of lithium bromide on the folding of proteins. They have made the very interesting suggestion that concentrated lithium bromide stabilizes the helix. Thus, serum albumin can be heated to  $95^\circ\text{C}$ . in 7.72 *M* lithium bromide without undergoing any change in optical rotation, and clupein and both oxidized and native ribonuclease are considerably less levorotatory in strong lithium bromide than in water. Schellman & Harrington ascribe this action of lithium bromide to the very low activity of the water that is present in these solutions.

All of these results seem to indicate that a process that is in a sense the opposite of a denaturation is possible in native proteins. We shall come back to this again in discussing the recent work of Yang & Doty.

*Rotatory dispersion.*—The quantum mechanical and classical theories of optical rotatory power agree that the dependence of the optical rotation,  $[\alpha]_\lambda$ , measured with light of wavelength  $\lambda$  should vary with  $\lambda$  according to the relation

$$[\alpha]_\lambda = \sum K_i/(\lambda^2 - \lambda_i^2) \quad 1.$$

where  $\lambda_i$  is the wavelength of the  $i$ th absorption band of the molecule,  $K_i$  is a constant (which may be positive or negative) characteristic of the  $i$ th band, and the sum is taken over all of the absorption bands belonging to the molecule. If the absorption occurs over a range of wavelengths, as is invariably the case with organic molecules, the sum should be replaced by an integral, but as long as measurements are made at wavelengths not too close to the absorption regions, equation 1 should be accurate. According to equation 1,  $[\alpha]_\lambda$  should become very large as one approaches an absorption band, and it should change sign on passing through the band. Equation 1 is called the Drude dispersion equation.

It is often found in practice that if one uses wavelengths that are longer than those of any of the absorption bands of the substance, then the dispersion can be quite accurately expressed by means of the simple equation

$$[\alpha]_\lambda = K/(\lambda^2 - \lambda_0^2) \quad 2.$$

where  $K$  and  $\lambda_0$  are constants. This result does not mean that a single absorption band is responsible for the optical rotation, as one might imagine. It is merely a consequence of the mathematical form of equation 1 that at long wavelengths it tends to approximate to the shape given by equation 2, the constants  $K$  and  $\lambda_0$  being functions of the  $K_i$ 's and  $\lambda_i$ 's (69, 85, 86). Substances whose dispersion is described accurately by equation 2 are said to show simple dispersion. Occasionally it is found that the dispersion in the visible and near ultraviolet cannot be described by a single Drude term, but that two terms must be retained,

$$[\alpha]_\lambda = K_1/(\lambda^2 - \lambda_1^2) + K_2/(\lambda^2 - \lambda_2^2) \quad 3.$$

If it should happen that  $K_1$  and  $K_2$  are opposite in sign, and if the absolute magnitude of  $K_1$  is greater than that of  $K_2$ , and if the constant  $\lambda_2$  is greater than  $\lambda_1$ , then at very long wavelengths ( $\lambda$  much greater than either  $\lambda_1$  or  $\lambda_2$ ), the first term in 3 will be larger than the second term, and the sign of the rotation will be the same as the sign of  $K_1$ . As the wavelength is decreased, however, and as  $\lambda$  approaches  $\lambda_2$ , the second term in 3 will eventually become larger than the first term.  $[\alpha]_\lambda$  will then reverse its sign, even though  $\lambda$  has not gone through any absorption band of the molecule. This type of behavior is called complex dispersion.

It has been found that both native and denatured proteins invariably



show simple dispersion [see Schellman & Schellman (86) for several measurements and for further references]. Linderstrøm-Lang & Schellman (60) have, however, observed that the constant  $\lambda_0$  in equation 2 always decreases slightly when a protein is denatured. This finding has been frequently confirmed [see, for instance, Yang & Doty (89)]. It provides us, therefore, with an additional empirical criterion for protein denaturation.

The rotatory dispersion of synthetic polypeptides has been studied by Yang & Doty (35, 89), Doty *et al.* (34), and Moffitt and Yang (69). These workers have made the very interesting observation that the helical forms of poly- $\gamma$ -benzyl-L-glutamate and poly-L-glutamic acid show complex dispersion, whereas the random coil forms show simple dispersion. Furthermore, although the numerical values of the optical rotations change considerably in going from one solvent to another, the dispersion remains simple in all solvents that yield random coils and it remains complex in all solvents that produce helices. It therefore appears that the helix gives rise to complex dispersion. If the helix is an important structural element in globular proteins, it is therefore surprising that the dispersion of native proteins is invariably simple. Furthermore, Yang & Doty have found that polypeptides in the helical form almost always have small positive values of  $[\alpha]_D$ , whereas native proteins are rather strongly levorotatory, as we have seen. Yang & Doty (89) argue from these two facts that only a relatively small portion of the polypeptide chains of native proteins can be folded into a helical conformation. They show that if a part of the polypeptide chain is folded into a helix having the complex dispersion observed for polyglutamic acid in its helical conformation, and if the remainder of the chain has a less regular conformation whose rotation and dispersion approximate that of the random coil form of polyglutamic acid, then, unless at least 50 per cent of the chains are in the helical form, the dispersion observed with the mixture will be simple at the wavelengths ordinarily used in dispersion measurements on proteins. They note, however, that in such mixtures the dispersion constant  $\lambda_0$  in equation 2 increases as the fraction of helical form present is increased from zero to 50 per cent. In this way they are able to account for the observation of Linderstrøm-Lang & Schellman (60) that was mentioned in the last paragraph. By comparing the values of  $[\alpha]_D$  and  $\lambda_0$  of native proteins with the values expected from hypothetical mixtures of random coils and helices, Yang & Doty estimate that among the common native proteins such as ovalbumin, ribonuclease, and serum albumin only approximately 15 to 40 per cent of the polypeptide chain is folded as a helix. These arguments are strongly supported by the finding that when proteins are dissolved in non-aqueous solvents known to induce the formation of helices in synthetic polypeptides, the optical rotation becomes considerably less levorotatory than the values found for the native proteins in water. In two instances—silk fibroin and the oxidized B chain of insulin (neither of which contain any disulfide cross linkages that might interfere with helix formation)—it was

possible to produce both the complex dispersion and the positive values of  $[\alpha]_D$  that are characteristic of helices formed from L-amino acid polymers. Yang & Doty have also compared the behavior of several proteins in these solvents before and after rupturing the cystine cross linkages that are present in the molecule. In this way they were able to show that these cross linkages interfere seriously with helix formation in insulin, that there is moderate interference in the case of serum albumin, but that the interference is negligible in ribonuclease.

A word of caution is in order concerning the interpretations of the changes of the optical rotation and of the dispersion that have been discussed above and in the previous section on optical rotation. These interpretations are based on the implicit assumption that if the polypeptide chains in the native protein fold in any other way than as helices, then this fold must be quite irregular, so that its contribution to the optical rotation is effectively the same as if it were a random coil. (This does not mean, of course, that the postulated nonhelical folding in native proteins must have the flexibility of a random coil; indeed, it may be just as rigid as the helix, as long as the pattern is not regular.) This is a rather drastic assumption, and it may possibly be untrue. It is entirely conceivable, for instance, that some globular proteins contain regions in which the chains are arranged in a structure similar to one of the  $\beta$ -structures. There is no reason to believe that the contributions of such regions to the rotation of the molecule would necessarily simulate the contribution of a random coil. Yang & Doty (89) have, in fact, presented rotation and dispersion measurements on low molecular weight poly-gamma-benzyl-L-glutamate at different concentrations in chloroform. Both  $[\alpha]_D$  and the dispersion change considerably with the concentration, and in the most concentrated solution studied  $[\alpha]_D$  is positive. Furthermore, the dispersion is not simple, and the deviations from equation 2 are of a different character from the deviations observed for helices. Infrared evidence has already been mentioned which indicates that in concentrated solutions in nonhydrogen bonding solvents these low molecular weight polypeptides produce aggregates which resemble  $\beta$ -structures. The changes that take place in the optical rotation of collagen and gelatin when they melt may also be mentioned in this connection. Boedtker & Doty (19) have shown that this process is akin to a denaturation in that the regular pattern of folding of the collagen chains appears to be replaced by something resembling a random coil. The process is accompanied by a large change in optical rotation, but it is in the opposite direction to the change observed in ordinary denaturation [ $[\alpha]_D$  = more than  $-300^\circ$  for the cold gel and the native collagen, and about  $-100^\circ$  for the molten gel and the unfolded collagen (22, 39)]. Furthermore, Carpenter & Lovelace (20) and Cohen (22) have found that the dispersion is simple for both hot and cold forms, and that  $\lambda_0$  is not changed on melting or unfolding. Collagen is, therefore, an example of another polypeptide structure with optical rotatory properties markedly different from those of the random

coil and of the  $\alpha$ -helix. (Since a large proportion of proline and hydroxyproline is needed in order to stabilize the collagen structure, however, it is not likely to be important in noncollagenous proteins.)

Until it is definitely known that regular structures other than helices do not occur in proteins, speculations based upon a one-to-one correlation between optical rotation or dispersion and the amount of helical form present in a protein must therefore be taken with some reservations. The assumption does, however, make a very interesting and useful working hypothesis at the present stage of development of our understanding of protein structure, and it is not without substantial justification.

Certain basic principles of the theory of optical rotatory power have been disregarded in some recent discussions of the changes in optical rotation that accompany the helix-random coil transition in polypeptides. Optical rotatory power differs from molecular properties, such as the dipole moment, the polarizability, the molecular volume, and the absorption spectrum, in that it cannot usually be broken down into a sum of contributions by individual atoms or groups of atoms in the molecule. All modern theories of optical rotatory power agree that optical rotation must be regarded as the sum of contributions resulting from the mutual interactions of the various groups present in the molecule [see, for example, the discussion by Kauzmann (54) and references cited therein]. Thus we cannot say that the optical rotation of, say, secondary butyl bromide,  $C_2H_5-CHCH_3-Br$ , is the sum of a contribution by the bromine atom, plus a contribution by the methyl group, plus a contribution by the ethyl group. At least to a first approximation the rotation is the sum of an effect produced by the methyl group on the bromine atom, plus an effect of the ethyl group on the methyl group, plus an effect of the bromine atom on the methyl group, and so on, considering each of the twelve possible interactions between the four groups attached to the asymmetric carbon atom. Therefore, in considering the optical rotation of the helical form of a polypeptide containing amino acids that have side chains, one can say that the optical rotation arises from (a) the sum of the interactions between groups present in the backbone of the helix, plus (b) the sum of the interactions of the side chains with each other, plus (c) the sum of the interactions of the side chains with the backbone of the helix, plus (d) the inherent rotations of the side chains (i.e., the rotations they would have if they were isolated from the helix and from each other). It is evidently quite wrong to suppose that the rotation of a helical polypeptide is made up of an inherent contribution of the helix plus another contribution from the side chains, and that these contributions can be separated. When the helix is destroyed, not only is the contribution of the polypeptide backbone altered [interactions of type (a)] but so are contributions (b) and (c). Contribution (d) might remain unchanged if the side chains do not change their conformations when the helix is destroyed, but even this is far from likely, especially if the side chains are at all bulky. It is equally wrong to consider the

optical rotation of a polypeptide helix as the sum of a contribution by the helix and a contribution by the asymmetric centers in the chain, because this neglects the interactions between the helix and the groups attached to the asymmetric centers, as well as the interactions of the centers with each other, both of which can be drastically changed if the helix is transformed into, say, a random coil. Clearly, then, the large changes in rotation that occur when helices are transformed into random coils must not be considered to be the result of a change in the polypeptide backbone alone. The change is just as much determined by the interactions between the backbone and the side chains, and by the interactions between the side chains. One might suppose that the side chains are too far apart or are too far from the helix to cause an appreciable interaction. It is known, however, that the interactions giving rise to optical rotation can extend over large distances. For instance, the optical rotation of 3-methyl-cyclopentanone has the very considerable value,  $[\alpha]_D = 130^\circ$ , and must arise largely from the interaction of the 3-methyl group with the carbonyl oxygen atom. The distance between the methyl carbon atom and the carbonyl oxygen is 4.7 Å. The side chains on an  $\alpha$ -helix can be much closer together than this and they can also be closer than this to the peptide linkages in the helix. Thus, there is reason for believing that the interactions of the side chains with each other and with the helix make a substantial contribution to the optical rotation.

Moffitt (67) has considered the optical rotation of a long helical coil from a quantum mechanical point of view. He points out that the interactions between a large number of identical chromophoric groups, such as the peptide linkages in the  $\alpha$ -helix, will spread each wavelength of light absorption into a band. He has shown that only two of the wavelengths in each band can contribute terms to the Drude expression, equation 1. If these two wavelengths are  $\lambda_1$  and  $\lambda_2$ , then the Drude expression must contain a pair of terms of the form

$$[\alpha]_{\lambda}' = \frac{\lambda_1^3}{\lambda^3 - \lambda_1^2} (a_1 + b) + \frac{\lambda_2^3}{\lambda^3 - \lambda_2^2} (a_2 - b) \quad 4.$$

where  $a_1$ ,  $a_2$  and  $b$  are constants. The constant  $b$  is determined by the interaction between identical groups located at different points along the helix, whereas  $a_1$  and  $a_2$  are determined by the interactions of these groups with other groups in the molecule and in the solvent. If we write  $\lambda_1 = \lambda_0 + \alpha$  and  $\lambda_2 = \lambda_0 + \beta$ , where  $\lambda_0$  is the wavelength of absorption of the groups in the absence of any mutual interactions and  $\alpha$  and  $\beta$  are the shifts caused by the interactions, and if we assume that  $\alpha$  and  $\beta$  are small compared with  $\lambda_0$ , then equation 4 can be rearranged into the forms,

$$[\alpha]_{\lambda}' = \frac{\lambda_0^3(a_1 + a_2) + 3\kappa\lambda_0^2}{\lambda^3 - \lambda_0^2} + \frac{2\kappa\lambda_0^4}{(\lambda^2 - \lambda_0^2)^2} \quad 5a.$$

$$= \frac{\lambda_0^3(a_1 + a_2) + \kappa\lambda_0^2}{\lambda^3 - \lambda_0^2} + \frac{2\kappa\lambda_0^2\lambda^2}{(\lambda^2 - \lambda_0^2)^2} \quad 5b.$$

where  $\kappa$  has been written for the quantity  $[\alpha a_1 + \beta a_2 + (\alpha - \beta)b]$ . Thus, dependence on the wavelength  $\lambda$  of the contribution by these two absorption frequencies can be expressed in the alternative forms,

$$[\alpha]_{\lambda}' = \frac{A}{\lambda^2 - \lambda_0^2} + \frac{B\lambda_0^2}{(\lambda^2 - \lambda_0^2)^2} = \frac{A'}{\lambda^2 - \lambda_0^2} + \frac{B\lambda^2}{(\lambda^2 - \lambda_0^2)^2} \quad 6.$$

Where  $A' = A - B$ . Moffitt could show that the term  $(\alpha - \beta)b$  in  $\kappa$  is much larger than  $\alpha a_1 + \beta a_2$ , so that  $B = (\alpha - \beta)\lambda_0^2 b$  very nearly, and  $B$  is a property of the isolated helix. Each of these expressions contains a term that is quite different from the terms appearing in the Drude equation, although, of course, not in conflict with it. Equations of this form are not, however, especially characteristic of helices, because they can also be obtained whenever a molecule contains a pair of identical and weakly interacting groups.<sup>4</sup>

Inspection of equations 6 reveals that when  $\lambda$  is much greater than  $\lambda_0$ , the sign of the optical rotation is determined by the sign of  $A$  or  $A'$ , whereas when  $\lambda$  approaches the value of  $\lambda_0$ ,  $B$  determines the sign of the rotation. Thus, if  $A$  and  $B$ , or  $A'$  and  $B$ , are opposite in sign, complex dispersion will be observed. According to Moffitt, this is the origin of the complex dispersion of polypeptides when they are in the helical conformation. Moffitt & Yang (69) have shown that the observed dispersion of the  $\alpha$  forms of polypeptides fit equation 6 very closely. Furthermore, the constants  $B$  and  $\lambda_0$  are not affected by the solvent, although the constant  $A$  varies considerably from one solvent to another. This is what we should expect if the value of  $B$  is determined entirely by interactions within the helix. It should be mentioned,

<sup>4</sup> This is easily shown in the following way. Let two identical groups interact and consider only the contributions of the transition to a single excited level in each of the groups. Let the wavelength of this transition be  $\lambda_0$  when the groups do not interact. When the groups do interact the excited level will be split into two levels and absorption will occur at the two wavelengths  $\lambda_1$  and  $\lambda_2$  instead of at  $\lambda_0$ . These transitions will, therefore, contribute two terms to the Drude expression, which will have exactly the same form as equation 3. If the mutual perturbation of the two groups is large compared with the perturbations induced by other transitions and other groups, the sum rule for rotatory strengths (54, p. 711) can be applied to the two terms in the numerators of equation 3, which must therefore be related as follows:

$$(K_1/\lambda_1^2) + (K_2/\lambda_2^2) = 0$$

When this relation is substituted into equation 3, assuming that  $\lambda_1$  and  $\lambda_2$  are not very different from  $\lambda_0$ , one finds that there is a contribution to  $[\alpha]_{\lambda}$  given by

$$\frac{[K_1(\lambda_1 - \lambda_2)/\lambda_0]}{(\lambda^2 - \lambda_0^2)^2} \lambda^2$$

which has the same dependence on  $\lambda$  as the second term in equation 5b. If other groups in the molecule also perturb the identical pair an additional term of the form  $A/(\lambda^2 - \lambda_0^2)$  will be present, and the contribution of the group will have the same form as equations 5b and 6.

however, that Yang & Doty (89) find that the observed dispersion can be fit equally well by two Drude terms as in equation 3, the value of  $\lambda_1$  being decidedly different from the value of  $\lambda_2$ ; it is, in fact, almost impossible to decide between these two equations on the basis of a fit to experimental points that do not involve measurements quite close to the wavelength  $\lambda_0$ . Furthermore, Moffitt & Yang have not made any allowance for contributions to the rotation of the molecule by transitions that take place at wavelengths other than  $\lambda_0$ . At the very least these additional transitions will add other terms of the form  $K_i/(\lambda^2 - \lambda_i^2)$  to the expression for  $[\alpha]_\lambda$ ; such contributions are surely present and there is no reason to believe that they will be small. Thus, the choice of the same value of  $\lambda_0$  in both terms in equations 6 is an unnecessarily rigid assumption whose only justification seems to be that it reduces the number of free parameters and, thus, makes it easier to obtain values for the constants  $B$  and  $b$ . The constants obtained in this way are therefore probably somewhat in error, though it is doubtful if this error is very serious. Above all, it must be emphasized that the agreement between the observed dispersion and equation 6 cannot be taken as compelling independent evidence for the presence of helices in polypeptides, since the same type of dispersion can arise in several other ways.

More recently Moffitt (68) has made a theoretical estimate of the value of the constant  $B$ . He assumes that it arises entirely from the interaction of the peptide linkages in the chain. Interactions involving two strong absorption bands at 1480 Å and 1850 Å are considered. Each band gives rise to a term of the form  $B_i/(\lambda^2 - \lambda_i^2)^2$ , the values of  $\lambda_i$  being those just mentioned. Under certain conditions these two terms may act together as if they were a single term of the same form with  $\lambda_0 = 2000$  Å. and  $B$  very close to the value obtained by fitting the observed dispersion data to equation 6. On the basis of the agreement (which it must be admitted is not obtained without making several somewhat questionable assumptions), Moffitt concludes that the helix in the  $\alpha$  forms of polymers of L-amino acids is right handed.

Fitts & Kirkwood (40) have calculated the contribution of the helix to the optical rotation of a polypeptide using Kirkwood's theory of optical rotation. They subsequently assumed (41) that the change in the rotation that occurs in the helix-coil transition is entirely due to the disappearance of the contribution of the helix and can be equated to the calculated value for the rotation. They concluded that the  $\alpha$ -helix in poly-L-amino acids is right handed, in agreement with Moffitt. Reasons for doubting the adequacy of this assumption have, however, been discussed above. Furthermore, Kirkwood's theory is known to omit certain contributions involving weak absorption bands that make large contributions to the optical rotation (54, p. 721-22). In addition, the assumptions made by Kirkwood & Fitts, regarding the spatial orientations and the symmetry of the polarizability ellipsoid of the peptide link, have been questioned by Moffitt (68). Thus, there appears to be some reason to doubt the significance of this calculation.

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## BOND ENERGIES

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### INTRODUCTION

*Prior review articles.*—The only article on bond energies in *Annual Reviews* is that by Glockler (71), which covered the developments in this field up to 1951. Cottrell's excellent and comprehensive book *The Strengths of the Chemical Bonds* (44) appeared in 1954. This book gives a complete picture of the whole subject up to the middle of 1953. Experimental methods for determining bond dissociation energies in diatomic and polyatomic molecules are discussed in great detail together with the methods for determining the heats of formation of molecules and free radicals. The reliability and accuracy of the various methods are critically examined, and lists of values of bond dissociation energies, heats of atomization, internuclear distances, and force constants are included. Also in 1954 appeared Steacie's monumental monograph on *Atomic and Free Radical Reactions* (158), in which a chapter on bond dissociation energies was included. In spite of the relative brevity of the chapter, the various terms related to the concept of bond strength were clearly defined, the limitations of the experimental techniques used were pointed out, and comprehensive tables were included listing values of bond dissociation energies—primarily in organic molecules—which appeared in the literature up to September 1953.

More recently, Trotman-Dickenson (171) has critically discussed in a monograph on *Gas Kinetics* the different kinetic methods used for the determination of bond dissociation energies and the assumptions underlying these methods. The literature was surveyed up to July 1954, and values for bond dissociation energies in many organic molecules were listed.

Knowledge of bond strengths in molecules is of fundamental importance in chemical kinetics, particularly in providing a basis for postulating reasonable mechanisms for gas phase reactions. Hence one is not surprised to find data on bond dissociation energies and related molecular and thermochemical parameters in review articles dealing primarily with other topics. The reader is referred to the recent reviews by Davidson & Sowden (46) and by Porter (125) on reaction kinetics in gases, by Sponer (156) on spectroscopy, by Bawn & Tipper (13) on combustion and flames, and by Brewer & Searcy (21) on high temperature chemistry.

*Scope of this review.*—In the present review, we hope to have covered the main contributions in the experimental field made over the period of 1954 to December, 1956. Inevitably some earlier literature will also be cited. In all

probability some important papers have been overlooked; for this our apologies are offered to their authors and to the reader. Our task in reviewing the literature has been somewhat easier than might be expected since no major innovation in experimental techniques or in the interpretation of the results has been made since the publication of Cottrell's book. Discussion of the various papers were kept, therefore, to a minimum, except on points of controversy or ambiguity where we felt compelled to express our opinion. In some cases, where no other data were available, average bond energies have been given. The terms used are identical to those defined by Szwarc (163) and accepted by Cottrell (44). Although the heats of formation of radicals are derived from thermochemical data and relevant bond dissociation energies, the recent advances in thermochemistry have not been reviewed here. Sufficient to say that it is encouraging to find that great progress has been made in the techniques of bomb calorimetry of sulfur- (161, 175), halogen- (15, 72) and metal-organic compounds (145; see also 48). In recent years reaction calorimetry also has been further developed for the determination of the heats of formation of organic compounds containing halogens (25), phosphorus (35, 120), arsenic (117), boron (154), and mercury (36).

#### HEATS OF DISSOCIATION OF $N_2$ AND CO AND HEAT OF SUBLIMATION OF CARBON

Among the most difficult problems which have attracted a great deal of interest, effort, and controversy over the last few decades have been the dissociation energies of  $N_2$  and CO molecules, and the thermochemically related heat of sublimation of carbon. Various authors at different times have recommended widely differing estimates for these physical constants. The suggested values for  $D(N_2)$  were 7.383, 8.573, 9.764 and 11.8 ev, and those for  $D(CO)$  were 6.92, 9.14, 9.61 or 11.11 ev. The main controversy has been due to the difficulty of reaching a unanimous interpretation of the spectra of these two diatomic molecules (80). This problem was fully discussed by Gaydon (65).

In 1951 Kistiakowsky *et al.* (90) claimed they had evidence for  $D(N_2) = 9.765$  ev (or  $\sim 225$  kcal./mole) from their study of the stationary detonation waves of a cyanogen-oxygen mixture. They also stated that this value for  $D(N_2)$  leads to a value of 170 kcal./mole for  $L(C)$  and to  $D(CO) = 11.1$  ev (or  $\sim 256$  kcal./mole). Since 1951, a number of data based on independent and unrelated experimental results have been published supporting the high values of  $D(N_2)$  and  $L(C)$ . Frost & McDowell (64) have confirmed  $D(N_2) = 9.765$  ev from their electron impact study of the dissociation of  $N_2$  by essentially monoenergetic electrons. By a similar method, Lagergren (93) arrived at a value of 11.1 ev for  $D(CO)$ . Brackett (19) reinterpreted previous electron impact data for CO and concluded that they indicate the high value for  $D(CO)$ .

Chupka and co-workers (85) presented a complete review of their elegant method for the determination of dissociation energies from thermodynamic

equilibria studied by means of mass spectrometry. Chupka *et al.* (39) determined the composition of the vapour in equilibrium with carbon in a Knudsen cell at 2500°K. The vapour consisted of  $C(g)$ ,  $C_2(g)$ , and  $C_3(g)$ , and the calculated heats of sublimation of these species were found to be 171, 190, and 200 kcal., respectively.

A review of this topic up to 1955 is found in Brewer & Searcy's article (21). As pointed out by these authors no other problem in chemistry has been subjected in recent years to such a searching examination. Apparently a complete agreement has been reached on these three basic values. A recent review article dealing with the determination of  $L(C)$  has been published by Kern (87). Some new evidence on the spectroscopy of CO has been published recently by Tanaka, Jursa & LeBlanc (182).

It is quite unfortunate that Cottrell used in his book (44) the lower values for the heats of atomization of carbon and nitrogen, namely  $L(C) = 138$  kcal./gm. atom and  $D(N_2) = 170$  kcal./mole. Therefore, the bond energy terms derived in his book for compounds containing carbon, nitrogen, or both require revision in the light of the now universally accepted higher values for  $L(C)$  and  $D(N_2)$ .

#### DIATOMIC MOLECULES

At present one cannot decide which of the three spectroscopic values—76, 83, or 102.5 kcal./mole—for  $D(S_2)$  is the correct one (68, 107). The problem has been discussed at length by Gaydon (65). St. Pierre & Chipman's (157) investigation of the equilibrium in  $SO_2$  or  $SO_2$ -CO mixtures at 1550°K. led them to propose  $D(SO) = 118.7$  kcal./mole, and  $D(S_2) = 83$  kcal./mole. Difficulties in the interpretation of the SH spectrum prevent a decision to be reached for  $D(SH)$ , from which  $\Delta H_f(S)$  and  $D(S_2)$  could be derived (149).

The investigation of the rotational structure of the Schumann-Runge absorption bands of  $O_2$  led Brix & Herzberg (23) to propose  $D(O_2) = 117.96 \pm 0.04$  kcal./mole. Hornbeck (82) has recalculated the dissociation energy of the OH radical at 4.629 eV = 106.5 kcal./mole from spectroscopic data. This value is higher than the older estimate of 100.2 kcal. (52) and seems doubtful in view of the recent careful spectroscopic analysis by Barrow leading to a value of 101.48 kcal. (8) or  $101.3 \pm 0.3$  kcal. (7). In spite of the thorough analysis of the spectrum of CN from 2,000 to 10,000 Å, Douglas & Routly (51) have not been able to arrive at a definite value for  $D(CN)$ . A reinvestigation of the spectrum led Carroll (31) to suggest a probable value of 8.2 eV for  $D(CN)$ . Durie & Ramsay (135) have calculated an upper limit of 62.8 kcal./mole for  $D(IO)$  from the observed predissociation limit in the absorption spectrum. The same authors state that there are two possible values for  $BrO$ , viz. 47.5 or 58 ( $\pm 2$ ) kcal./mole. Recently Wicke & Franck (177) reviewed the overwhelming evidence for  $D(F_2) = 37.4 \pm 1$  kcal./mole. Wise (178) obtained a similar value of  $37.6 \pm 0.8$  kcal./mole from effusion experiments. Wray & Hornig (179) claimed a slightly different value of  $31 \pm 4.3$  kcal./mole, derived from shock wave experiments. Palmer & Hornig (123) studied the

dissociation of bromine by shock waves [ $D(\text{Br}-\text{Br})=45$  kcal./mole] and obtained from this study valuable information on the energy transfer process leading to the dissociation act. The latter problem has been also treated by Davidson *et al.* (22), who have shown that the recombination of the atoms or radicals produced by shock waves has a slight negative temperature coefficient. Therefore, values of bond dissociation energies calculated by this method are several calories higher than the activation energy of the reaction leading to dissociation. Brodersen & Sicre (26) derived  $D(\text{BrF})=2.384$  ev from analysis of the absorption spectrum of BrF. In a study of the synthesis of phosphorus nitrides, Huffman *et al.* (83) calculated  $D(\text{PN})=7.1 \pm 0.05$  ev from the determination of the gaseous equilibrium between PN and  $\text{N}_2$  and  $\text{P}_2$ .

In recent years considerable interest has been stimulated for the study of the dissociation of inorganic oxides, hydroxides, hydrides, or salts at temperatures as high as 2400°K. (33, 94). These temperatures are attained by burning fuels such as hydrogen or acetylene, which are suitable solvents for the metallic compounds undergoing dissociation. The elements liberated at these high temperatures combine with the various components of the flame gases, including halogens if the latter are incorporated in the combustible mixture. The concentrations of the different components in the flames are obtained by measurement of the intensity of the emission spectrum of each component, and dissociation equilibria constants can be readily calculated from these data. In a recent paper, Sugden (160) surveyed critically the kinetic and thermodynamic bases of these methods and the experimental difficulties encountered, such as the determination of the correct flame temperatures and of the absolute concentrations of atoms or radicals. Reference to prior work is given (155). This paper is followed by a series of two papers on the dissociation of gaseous cuprous hydride (27) and hydroxide (28),  $D(\text{Cu}-\text{H})=66 \pm 2$  kcal./mole, and  $D(\text{Cu}-\text{OH})=61 \pm 4$  kcal./mole. Sugden (160) states that subsequent work from his laboratory will deal with molecules such as TiH, CaOH, BaOH, CaO, SrO, SrOH, BaO, and PbO. Studies of a similar nature were conducted by Lagerquist & Hultdt (94), Barrow *et al.* (9, 10), Gaydon (66), and Veits & Gurvich (173, 174). Some of the more recent values (in kcal./mole) calculated by these workers are  $D(\text{Si}-\text{O})=185 \pm 6.8$  (10),  $D(\text{Ge}-\text{O})=155.8 \pm 5.3$  (10),  $D(\text{Sn}-\text{O})=126.4 \pm 4$  (10),  $D(\text{Al}-\text{F}) \sim 163$  (9),  $D(\text{Al}-\text{O})=133.5 \pm 3$  (174),  $D(\text{Mg}-\text{O})=100.0$  (173),  $D(\text{Ca}-\text{O})=114.8$  (173),  $D(\text{Sr}-\text{O})=111.0$  (173), and  $D(\text{Ba}-\text{O})=138.1$  (173).

Chupka, Inghram and colleagues applied their ingenious electron impact method to the determination of dissociation energies in metallic oxides. In this work the partial pressures of the gaseous species, assumed to be in equilibrium with the condensed phase, at temperatures as high as 2000°K. are determined by a combination of Knudsen effusion and mass-spectrometric techniques. Their work up to 1955 has been reviewed by Brewer & Searcy (21) and their recent data have been summarized at a recent symposium (85). Some of their data differ from the results obtained by flame photometry. They give  $D(\text{Sr}-\text{O})=83.6 \pm 5$  (126),  $D(\text{Mg}-\text{O}) < 90$  (126),  $D(\text{Ba}-\text{O})=130$

$\pm 5$  (84), and  $D(\text{La—O}) = 188 \pm 8$  kcal./mole (40). For zirconium dioxide, they calculated  $D(\text{Zr—O})$  in  $\text{ZrO} = 180.6$  kcal./mole, while the sum of the two  $\text{ZrO}$  dissociation energies in  $\text{ZrO}_2$  was 334 kcal./mole (41). A dissociation energy of 78.8 kcal./mole for  $\text{LiI}$  was derived by Friedman (63) by mass spectrometry, whereas from spectroscopic studies a value of 88.0 kcal. is obtained.

#### MOLECULES CONTAINING BORON AND PHOSPHORUS

Boron chemistry along with inorganic chemistry in general has received much attention within recent years. Some average bond energy data have been obtained for boron and phosphorus compounds. McCoy & Bauer (113) have derived  $\Delta H_f(\text{BH}_3)$  by measuring the heat of reaction of diborane with methylamines. From these data, and on the basis of  $L(\text{B}) = 140.9$  kcal./g. atom (146), they calculated the bond energy term  $E(\text{B—H}) = 93.1$  kcal., in excellent agreement with the value proposed by Skinner (154). The latter obtained also the bond energy terms  $E(\text{B—F}) = 154.8$ ,  $E(\text{B—Cl}) = 108.5$ , and  $E(\text{B—Br}) = 90.2$  kcal. in compounds of the type  $\text{BX}_3$ . Mackenzie has calculated the  $\text{B—O}$  bond energy term at 100 kcal. in  $\text{B}_2\text{O}_3$  (111). It is doubtful whether this calculation is justified in view of the obvious difference in the nature of the  $\text{B—O}$  bonds in the  $\text{B}_2\text{O}_3$  molecule.

From heats of hydrolysis of phosphorus halides and of the oxidation of compounds containing trivalent phosphorus, Neale & Williams (120) calculated the following energy terms:  $E(\text{P—Cl}) = 80$ ,  $E(\text{P—Br}) = 65$ ,  $E(\text{P—OH}) = 105$ ,  $E(\text{P—F}) = 120$ ,  $E(\text{P—OP}) = 96$ ,  $E(\text{P—H}) = 78$  kcal. They assumed that the contribution of  $E(\text{O=P})$  to the total heat of formation was 115 kcal./mole irrespective of the molecule. They agree, however, that their values might require further verification in view of the unreliability of the accepted heats of formation of the parent compounds. More recently, these workers (121) have studied calorimetrically the conversion of tervalent and quinquevalent phosphorus halides to esters. The bond energy terms of the  $\text{P—OR}$  bonds in quinquevalent esters are found to be slightly larger than in the corresponding tervalent compounds.

#### BOND ENERGIES IN SOME ORGANO-METALLIC AND ORGANO-METALLOID COMPOUNDS

It seems appropriate at this point to present some data on bond energy terms for some organo-metallic and -metalloid compounds. Skinner's laboratory seems to have been one of the most productive in this field. His earlier work is reviewed in Cottrell's book (44). More recently from the thermochemistry of organophosphorus compounds, Chernick, Skinner & Mortimer (34) have obtained  $E(\text{P—OMe}) = 79.2$  kcal. and  $E(\text{P—OEt}) = 81.7$  kcal. in trimethyl and triethyl phosphites. In contrast to the assumed constant value of 115 kcal./mole for  $E(\text{O=P})$  by Neale & Williams (120), Chernick & Skinner (35) have calculated for  $D(\text{O=PX}_2)$  a value of 138 kcal./mole in tripropyl and tributyl phosphine, and a value of 151 kcal./mole in triethyl



phosphate. These workers point out that  $D(\text{O}=\text{PR}_3)$  may depend appreciably on the nature of the R group, in conformity with the ideas of Swarc & Evans (164) that the dissociation energy of a bond depends on its entire molecular environment and, therefore, generally is not a constant in a series of similar molecules. In this particular case, the dissociation process would involve the rupture of the  $\text{O}=\text{P}$  bond, which is most likely associated with a change in the valency state of the P atom and with a reorganization in the  $\text{PR}_3$  fragment of the  $\text{OPR}_3$  molecule. It is to be noted that these data might require some corrections in view of possible errors in the analysis of the reaction products. Tannenbaum & Schaeffer (170) have calculated the heat of formation of tributyl boron from which they derived  $E(\text{B}-\text{Bu}) = 70$  or 85 kcal., depending on whether  $L(\text{B})$  is assumed to be 97 or 140 kcal./g.atom. The value of 85 kcal. for  $E(\text{B}-\text{Bu})$  compares well with the value of 89 kcal. obtained by Skinner & Smith (154) for  $E(\text{B}-\text{Me})$ . Skinner & Smith calculated also  $E(\text{B}-\text{OEt})$  and  $E(\text{B}-\text{NMe}_2)$  at 119.3 and 104.3 kcal., respectively.

Long & Sackman have determined the heats of formation of trimethyl compounds of bismuth (101), antimony (102), and arsenic (103) by combustion calorimetry. Their values for the different bond energy terms in these compounds are  $E(\text{Bi}-\text{C}) = 33.8$ ,  $E(\text{Sb}-\text{C}) = 49.7$ , and  $E(\text{As}-\text{C}) = 51.5$  kcal. These workers (100) have also determined  $E(\text{P}-\text{C})$  in  $\text{PMe}_3$  and  $E(\text{Ga}-\text{C})$  in  $\text{GaMe}_3$  at 65.4 and 57.0 kcal./mole, respectively. All these determinations are somewhat uncertain in view of the difficulty of preparation of very pure starting materials, of the analysis of combustion products, and because of the tendency for incomplete combustion.

#### MISCELLANEOUS DATA

Gray & Waddington (78, 79) surveyed the thermochemistry of some azides and derived a value of 116 kcal./mole for the heat of formation of the azide radical,  $\text{N}_3$ . This leads to  $D(\text{H}-\text{N}_3) = 97 \pm 4$  kcal./mole in hydrazoic acid and to an average value of  $\sim 83$  kcal./mole for  $D(\text{C}-\text{N})$  in a few organic azides. They estimated also  $D(\text{N}-\text{H})$  in  $\text{NH}_3$ ,  $\text{NH}_2$ , and  $\text{NH}$ . Their results are similar to those published by Altshuller (2) i.e.,  $D(\text{NH}_2-\text{H}) = 104 \pm 2$ ,  $D(\text{NH}-\text{H}) = 88 \pm 4$ , and  $D(\text{N}-\text{H}) = 88 \pm 2$  kcal./mole. On the assumption that the gradation of the  $\text{N}-\text{F}$  bond strengths in  $\text{NF}_3$ ,  $\text{NF}_2$ , and  $\text{NF}$  is similar to that of  $\text{N}-\text{H}$  bonds in  $\text{NH}_3$ ,  $\text{NH}_2$ , and  $\text{NH}$ , Reese & Dibeler (138) suggested the values  $D(\text{NF}_2-\text{F}) = 73$ ,  $D(\text{NF}-\text{F}) = 62$ , and  $D(\text{N}-\text{F}) = 62$  kcal./mole. Sunner (161) derived bond energy terms in sulfur compounds, i.e.,  $E(\text{C}-\text{S}) = 61.5$ ,  $E(\text{S}-\text{H}) = 87.5$ ,  $E(\text{C}=\text{S}) = 115$ ,  $E(\text{S}-\text{S}) = 67$  kcal. However, it is to be noted that he used in his calculations the high value of 66.3 kcal./gm.atom for  $\Delta H_f^\circ(\text{S})$  and the low value of 138 kcal./gm. atom for  $L(\text{C})$ . Rutner *et al.* (142a) have calculated the thermodynamic functions of cyanogen and the equilibrium constant for the reaction  $\text{C}_2\text{N}_2 \rightleftharpoons 2\text{CN}$  between 1000° and 4500°K. From their data one obtains  $D(\text{NC}-\text{CN}) = 112$  kcal./mole. Tanaka & Watase (169a) have determined the heats of formation of some methoxy-polysilanes and polysiloxanes, and estimated the  $\text{Si}-\text{O}$  bond energy terms in these compounds at  $\sim 101.5$  kcal.

## KINETIC METHODS

In this section we propose to present the diverging results for  $D(\phi\text{CH}_2\text{—H})$  in toluene and to discuss the status of the toluene-carrier technique as well as the results obtained by other kinetic methods.

Since the publication of Szwarc's paper (162), in which he claimed that  $D(\phi\text{CH}_2\text{—H})$  is  $77.5 \pm 1.3$  kcal./mole, a number of other workers have re-determined this value by a variety of techniques. Some have confirmed this value, while others have obtained higher values. Schissler & Stevenson (143) derived a value of  $77 \pm 3$  kcal./mole from their measurements of appearance potential of the  $\text{C}_7\text{H}_7^+$  ion, assumed to be the benzyl ion, in mass spectra of toluene, ethylbenzene and dibenzyl and the appropriate thermochemical data. Subsequently, Field & Franklin (59) published results of their electron impact studies which were in excellent agreement with the value proposed by Szwarc and by Schissler & Stevenson. These data lead to a value of  $\sim 37$  kcal./mole for  $\Delta H_f(\phi\text{CH}_2)$ . Farmer *et al.* (54) criticized the conclusions of the previous mass spectrometric studies. Their main contention was that the directly determined value for the ionization potential of benzyl radical (105a) was lower by 0.7 eV ( $\sim 16$  kcal./mole) than that based on the data of Schissler & Stevenson. In a more recent paper, Farmer *et al.* (57) stated that the combination of the ionization potential of  $7.76 \pm 0.8$  eV for benzyl radical proposed by Lossing *et al.* (105a) with Schissler & Stevenson's appearance potential of  $11.87 \pm 0.1$  eV for the benzyl ion from toluene would lead to  $D(\phi\text{CH}_2\text{—H}) \leq 95$  kcal./mole. They also stated that this value seemed unreasonably high in view of the stability of the benzyl radical and suggested that either the appearance potential of the  $\text{C}_7\text{H}_7^+$  ion from toluene contained an excess energy term, or that the measured ionization potential of benzyl radical was too low by about 0.8 eV. On the other hand, the same group of workers (106), using the direct mass spectrometric method and their value for  $I(\phi\text{CH}_2)$ , estimated  $D(\phi\text{CH}_2\text{—Br})$  at  $44.7 \pm 3$  kcal./mole, which is a slightly lower value than that of  $50.5 \pm 2$  kcal./mole proposed by Szwarc *et al.* (165). The good agreement between these two values for  $D(\phi\text{CH}_2\text{—Br})$  might be considered supporting, though not compelling evidence for the value of  $I(\phi\text{CH}_2)$  proposed by Lossing *et al.* However, one is still at a loss to explain the discrepancy between the electron impact values for  $D(\phi\text{CH}_2\text{—H})$ .

In a very recent investigation, Rylander *et al.* (183) indicated that a possible explanation for this discrepancy might be that toluene under electron impact does not yield the benzyl<sup>+</sup> ion but the isomeric tropylium<sup>+</sup> ion. Such rearrangements of ions were previously discussed (e.g. 184) and even the phenyl<sup>+</sup> ion was considered capable of rearrangement by ring cleavage (185). Nonetheless, Schissler & Stevenson's value of  $77 \pm 3$  kcal./mole for  $D(\phi\text{CH}_2\text{—H})$  might still be correct provided the  $\text{C}_7\text{H}_7^+$  ion produced from toluene, ethyl benzene, and dibenzyl in their electron impact studies was the same ionic species containing the same amount, if any, of excess energy.

In an extension of their kinetic studies on the photobromination of hydrocarbons, Anderson, Sheraga & Van Artsdalen (3) have investigated the photochemical and thermal bromination of toluene and derived  $D(\phi\text{CH}_2\text{—H})$

= 89.5 kcal./mole. These reactions follow the pattern of the classical reaction between  $H_2$  and  $Br_2$ . The other  $D(C-H)$  values obtained by this method are listed in Steacie's monograph (158), except the later value of 89.6 kcal./mole for  $D(C-H)$  in isobutane (53). The high value of  $D(\phi CH_2-H)$  is arrived at by Anderson *et al.* on the assumption that the reaction between benzyl radical and  $Br_2$  (their reaction 3) has no activation energy. On the other hand, if this assumption is not valid,  $D(\phi CH_2-H)$  should be lower by whatever activation energy might be required for reaction 3. The assumption of zero activation energy for the reaction  $\phi CH_2 + Br_2$  is based on the analogy with the reaction between methyl radicals and  $Br_2$  (89). The latter reaction is exothermic to the extent of  $\sim 22$  kcal./mole, and this justifies the assumption of its activation energy being negligible. On the other hand, the reaction between benzyl radical and  $Br_2$  is only slightly exothermic ( $\sim 4$  kcal./mole). These estimates follow from the following data:  $D(CH_3-Br)$ ,  $D(\phi CH_2-Br)$  and  $D(Br_2)$  are 67.5 (147), 50.5 (165) and 45 (141) kcal./mole, respectively.<sup>1</sup> Therefore, it is reasonable to expect that the reaction of benzyl radicals with bromine would be associated with some activation energy. Schumacher [quoted in (158)] has suggested for the analogous reaction between the  $CCl_3$  radical and  $Br_2$  an activation energy of 6 to 7 kcal. This reaction is almost as exothermic as the reaction  $\phi CH_2 + Br_2$ , since  $D(CCl_3-Br)$  is  $\sim 49$  kcal./mole. Similarly, it has been postulated (158) that reactions between  $C_2H_5Br$  or  $C_2H_5ClBr$  radicals with  $Br_2$  require an activation energy of 5 to 10 kcal. Therefore, the value of 89.5 kcal./mole of Anderson *et al.* (3) should be considered only an upper limit for  $D(\phi CH_2-H)$ , and it would seem that a value of the order of 83 kcal./mole might be more acceptable. Benson & Buss (14a) have recently pointed out a number of fallacies in the kinetics of photobromination which would invalidate the mechanism proposed for these reactions.

Blades, Blades & Steacie (17) have reinvestigated the pyrolysis of toluene. Using deuterated toluene they obtained evidence (16) confirming the mechanism for the decomposition of toluene proposed by Szwarc. However, contrary to Szwarc, they concluded from their kinetic data that the rates of the decomposition were sensitive to surface conditions and that the pyrolysis deviates from first-order kinetics. Although they refrained from assigning a value to the C—H bond dissociation energy, they stated that the Arrhenius plot of an assumed first-order rate constant led to an activation energy of 90 kcal. However, their experiments were performed at higher temperatures than those used in Szwarc's study (165). In all probability the contribution of side reactions is more significant at higher temperatures and this might be the reason for the higher activation energy determined by these workers.

Benson & Buss (14, 29) have surveyed recently all the values derived for  $\Delta H_f(\phi CH_2)$ . Their paper is disappointing and confuses the issue. However, their conclusion that the value for  $D(\phi CH_2-H)$  proposed by Szwarc is

<sup>1</sup> If we accept  $D(\phi CH_2-Br) \sim 45$ , as proposed by Lossing *et al.* (106), the reaction  $\phi CH_2 + Br_2$  would be thermoneutral.

too low seems to be justified. To settle this point they made a resourceful attempt by a thermochemical approach. They investigated the equilibrium for the reaction  $\phi\text{CH}_3 + \text{Br}_2 \rightleftharpoons \text{CH}_2\text{Br} + \text{HBr}$ , deduced a reasonable value for the change in entropy of this reaction, and thus derived the corresponding change in the enthalpy,  $\Delta H = -8.0 \pm 1.2$  kcal./mole. This value represents the difference  $[D(\phi\text{CH}_2\text{—H}) - D(\phi\text{CH}_2\text{—Br})] - [D(\text{HBr}) - D(\text{Br}_2)]$ . Inserting the accepted values for  $D(\text{HBr})$  and  $D(\text{Br}_2)$  (180), they calculated the difference  $\Delta = [D(\phi\text{CH}_2\text{—H}) - D(\phi\text{CH}_2\text{—Br})]$  to be 33.7 kcal./mole. This is contrasted with the value 26.5 kcal./mole (corrected to 298°K.) for  $\Delta$  obtained from two independent kinetic studies. If the results of Benson & Buss are correct, and probably they are good within  $\pm 2$  kcal./mole and not a fraction of a kilocalorie as the authors claim, the discrepancy for  $\Delta$  amounting to about 7 kcal. could be apportioned among the corresponding C—H and C—Br bond dissociation energies. It is highly probable that the error in  $D(\phi\text{CH}_2\text{—Br}) = 50.5$  kcal./mole is small, if any (149, 163, 166, 186), and considering that the heat of reaction measured by Benson is correct, a value of 83 kcal./mole would seem appropriate for  $D(\phi\text{CH}_2\text{—H})$ .

The greatest part of Benson & Buss' paper is devoted to a review of the literature concerned with the heat of formation of benzyl radical and to a criticism of the kinetic method for determination of bond dissociation energies. They produced a table of values for the heat of formation of benzyl radicals, many of which were derived from impossible assumptions and obviously led them to fallacious results. For example, in spite of the published statements (32, 42, 128, 168) that the activation energies of the decompositions of benzyl-methyl-ketone and diacetyl must not be confused with the bond dissociation energies, this error has been introduced into the results given in their paper.

In their criticism of the kinetic method Benson & Buss (14) overlooked good and reliable experimental data and chose to emphasize two examples of the technique which are obviously the weakest and least reliable. Their mechanism for the decomposition of toluene is so general that it is of little value and it does not take into account the work of Blades & Steacie (16). Of course, the kinetic method, as other techniques, has its obvious limitations which have been clearly stated (168).

Lossing, Ingold & Henderson (106) calculated  $44.7 \pm 3$  kcal./mole for  $D(\phi\text{CH}_2\text{—Br})$  from their electron impact studies. Should this value be correct, then  $D(\phi\text{CH}_2\text{—H})$  would be 78.5 kcal./mole on the basis of the estimate of 33.7 kcal. for  $\Delta$  obtained by Benson & Buss. A final solution will have to come from independent experiments designed to settle the value for either  $D(\phi\text{CH}_2\text{—H})$  or  $D(\phi\text{CH}_2\text{—Br})$ , and for  $\Delta H_f(\phi\text{CH}_2\text{Br})$ . In our opinion the problem of  $D(\phi\text{CH}_2\text{—H})$  needs further independent verification. It seems probable that  $D(\phi\text{CH}_2\text{—Br}) \approx 50$  kcal./mole, and  $D(\phi\text{CH}_2\text{—H})$  would appear to be  $\sim 83$  kcal./mole.

Although the assumptions underlying the toluene-carrier technique have been questioned by some workers (14, 158), we believe that the technique, if properly used, is suitable for the determination of bond dissociation ener-

gies. A strong argument in favour of this technique is the good correlation between values obtained by this method and by other techniques. The essential conditions for a successful application of the toluene-carrier technique were outlined in a paper by Szwarc & Taylor (168).

Szwarc and co-workers have been continuing their studies of bond dissociation energies using the toluene-carrier technique. Rembaum & Szwarc (139, 140) determined the O—O bond dissociation energies in diacetyl, dipropionyl and dibutyryl peroxides to be 29.5, 30.0 and 29.6 kcal./mole, respectively. These values, in conjunction with the heats of formation of the respective peroxides and of the appropriate carboxylic acids, lead to  $D(\text{CH}_3 \cdot \text{COO} \cdot \text{H}) = 111.5$  kcal.,  $D(\text{C}_2\text{H}_5 \cdot \text{COO} \cdot \text{H}) = 109.5$  kcal.,  $D(\text{C}_3\text{H}_7 \cdot \text{COO} \cdot \text{H}) = 102.5$  kcal., and  $D(\text{OCOO} \cdot \text{H}) = 102$  kcal. (86a). Szwarc & Taylor (168) determined  $D(\text{CH}_3 \cdot \text{COCH}_3) = 72$  kcal./mole and calculated  $\Delta H_f(\text{CH}_3\text{CO}) = -10.8$  kcal./mole. Clark & Pritchard (42) confirmed these results and extended their studies to pyrolyses of higher ketones. The value  $\Delta H_f(\text{CH}_3\text{CO})$  of  $-10.8$  kcal./mole leads to  $D(\text{CH}_3\text{CO} \cdot \text{OCCH}_3)$  and  $D(\text{CH}_3\text{CO} \cdot \text{CH}_2\text{O})$ , of 56.6 and 50 kcal./mole, respectively. These two values are not in accord with the activation energies of 66 and 68 kcal./mole determined for the pyrolysis of diacetyl and phenylacetone (163); the reason for this discrepancy is discussed later. Szwarc & Taylor (167) derived  $D(\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{Cl}) = 68$  kcal./mole and  $D(\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{Cl}) = 73.2$  kcal./mole, and suggested values of 6.3 kcal./mole for  $D(\text{CO} \cdot \text{Cl})$  and  $\sim 96$  kcal./mole for  $D(\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{Cl})$ .

Recently a series of organic bromides and chlorides were studied in Szwarc's laboratories. The following results were obtained (186):  $D(\text{OCH}_2 \cdot \text{Br}) = 50.5$  kcal./mole;  $D(\text{OC}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{Br}) = 46$  kcal./mole;  $D(\alpha \text{ naphthyl} \cdot \text{CH}_2 \cdot \text{Br}) = 40$  kcal./mole;  $D(\beta \text{ naphthyl} \cdot \text{CH}_2 \cdot \text{Br}) = 45$  kcal./mole;  $D(\text{O}_2\text{CH} \cdot \text{Br}) = 44$  kcal./mole;  $D(9\text{-fluorenyl} \cdot \text{Br}) = 44.5$  kcal./mole;  $D(\text{O}_2 \cdot \text{CH} \cdot \text{Cl}) = 56$  kcal./mole;  $D(\text{O}_2\text{C} \cdot \text{Cl}) = 48$  kcal./mole. Studies of the pyrolysis of organic halides by the toluene carrier technique in Professor Semenov's laboratories led to the following results:  $D(\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{Cl}) = 59.3 \pm 2$  kcal./mole (187);  $D(\text{CCl}_3 \cdot \text{Cl}) = 55 \pm 3$  kcal./mole;  $D(\text{CH}_2 \cdot \text{CBr} \cdot \text{Br}) = 63 \pm 2$  kcal./mole (188).  $D(\text{CH}_3 \cdot \text{Cl})$  was estimated at 85.5 kcal./mole (188), apparently in the absence of toluene. Sehon & Darwent (150) and Braye *et al.* (24) studied the decomposition of some sulfur organic compounds by the toluene-carrier technique, and determined  $D(\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{SH}) = 53 \pm 2$ ,  $D(\text{CH}_3 \cdot \text{SH}) \simeq 67$ ,  $D(\text{C}_2\text{H}_5 \cdot \text{SH}) \simeq 63.5$ , and  $D(\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{SCH}_3) = 51 \pm 2$  kcal./mole. On the basis of thermochemical data they derived  $\Delta H_f(\text{SH}) = 32$  kcal./mole which leads to  $D(\text{H} \cdot \text{SH}) = 89 \pm 4$  kcal./mole (149).

Dissociation energies of some C—Hg bonds were determined by the toluene-carrier technique. The results are reviewed by Carter, Chappell, & Warhurst (32) and include the pyrolysis of  $\text{Hg}(\text{CH}_3)_2$  (73),  $\text{Hg}(\text{C}_2\text{H}_5)_2$ ,  $\text{Hg}(n\text{-C}_3\text{H}_7)_2$ ,  $\text{Hg}(iso\text{-C}_3\text{H}_7)_2$  (37),  $\text{Hg}(\text{Ph})_2$ ,  $\text{Hg} \cdot \text{Cl} \cdot \text{Ph}$ ,  $\text{Hg} \cdot \text{Br} \cdot \text{Ph}$ ,  $\text{Hg} \cdot \text{Cl}(n\text{-C}_3\text{H}_7)$  (32). Chilton & Gowenlock (37) deduced from their value of

$(D_1 + D_2) = 47.1$  kcal./mole in  $\text{Hg}(n\text{Pr})_2$ , a value of 98 kcal./mole for  $D(n\text{Pr}-\text{H})$ , which is in excellent agreement with values of about 99 kcal. derived by other methods (158). From thermochemical data, they calculated values for  $(D_1 + D_2)$  in zinc dialkyls; viz.,  $\text{Zn}(\text{Me})_2: 83.8 \pm 3.7$ ;  $\text{Zn}(\text{Et})_2: 67.4 \pm 5.4$ ;  $\text{Zn}(n\text{Pr})_2: 79.6 \pm 9.2$ ; and  $\text{Zn}(n\text{-Bu})_2: 83.1 \pm 12.8$  kcal./mole. Laurie & Long (95) determined  $D_1(\text{Hg}-\text{C})$  in  $\text{HgMe}_2$  at  $51.5 \pm 2$  kcal./mole by pyrolysis of  $\text{HgMe}_2$  in a static system. Preliminary results obtained in Trotman-Dickenson's laboratory (172) from the pyrolysis of cadmium dimethyl in a stream of toluene indicate that the  $D(\text{Cd}-\text{C})$  is  $\sim 45$  kcal./mole. This value is in fair agreement with  $D(\text{Me}-\text{CdMe}) = 43.5 \pm 1.2$  kcal./mole calculated by Long (100) from pyrolysis. Long also states that  $D(\text{Cd}-\text{Me})$  in the  $\text{CdMe}$  radical is  $21.1 \pm 4$  kcal./mole. Price & Trotman-Dickenson (127) are also investigating the thermal decomposition of  $\text{Zn}(\text{Me})_2$  and suggest that  $D_1(\text{Zn}-\text{C}) = 48 \pm 1$  kcal./mole and  $D_2(\text{Zn}-\text{C}) = 35 \pm 3$  kcal./mole, the sum of which agrees splendidly with the thermochemically expected value. Chernick, Skinner & Wadsö (36) have compiled the available data on the thermochemistry of diphenyl mercury and after a critical examination of the bond dissociation energy in phenyl derivatives arrived at an estimate of  $69 \pm 4$  kcal./mole for  $\Delta H_f(\text{C}_6\text{H}_5)$  in good agreement with the value obtained by Szwarc & Williams (168a). From this value in conjunction with  $\Delta H_f$  values for H atoms (180) and  $\text{C}_6\text{H}_6(\text{g})$  (181), one derives that  $D(\text{C}_6\text{H}_5-\text{H})$  is  $\sim 101$  kcal./mole. Ayscough & Emeleus (5) suggested that  $D(\text{As}-\text{C})$  in trimethylarsine was 54.6 kcal./mole, which is in good agreement with  $E(\text{As}-\text{C}) = 51.5$  kcal./mole (103), and that  $D(\text{As}-\text{C})$  in tris(trifluoromethyl)arsine was 57.4 kcal./mole.

Maccoll (110) has continued his studies of the pyrolysis of organic bromides. For the particular case of allyl bromide, he suggested that the initial reaction was the splitting of the  $\text{C}-\text{Br}$  bond and that the activation energy of 45 kcal./mole was in good agreement with the thermochemical value of 45.5 kcal./mole (141) for  $D(\text{CH}_2:\text{CH}\cdot\text{CH}_2-\text{Br})$ . Values of  $47.5 \pm 2$  and  $47.7 \pm 2.5$  kcal./mole were derived for this bond dissociation energy by the toluene-carrier technique and the electron impact method (165, 106). Pritchard *et al.* (131, 132) calculated  $D(\text{CF}_3-\text{H}) = 102 \pm 2$  kcal./mole from experimentally determined activation energies of the forward and backward reaction  $\text{CF}_3 + \text{CH}_4 \rightleftharpoons \text{CF}_3\text{H} + \text{CH}_3$  and the accepted value of  $102.5 \pm 1$  kcal./mole for  $D(\text{CH}_3-\text{H})$ . They estimated also  $\Delta H_f(\text{CF}_3\text{H})$  at  $-169$  kcal./mole by comparing the heats of formation of  $\text{CF}_3\text{Cl}$ ,  $\text{CH}_4$  and  $\text{CH}_3\text{Cl}$ , and derived  $\Delta H_f(\text{CF}_3) = -119$  kcal./mole and  $D(\text{CF}_3-\text{CF}_3) = 65$  kcal./mole. Their value for  $\Delta H_f(\text{CF}_3)$  is in excellent agreement with  $\Delta H_f(\text{CF}_3) = -120.5$  kcal./mole derived by Rabinovitch & Reed (134) from rates of reaction of sodium atoms with chlorofluoromethanes. Applying the Evans & Polanyi relation,  $\Delta D = \alpha \Delta H$ , Rabinovitch & Reed estimated  $D(\text{CF}_3-\text{Cl})$  at  $79 \pm 2$  kcal./mole on the basis of  $D(\text{CH}_3-\text{Cl}) = 81.2$  kcal./mole. From available thermochemical data, they calculated also  $D(\text{CF}_3-\text{F}) = 116.5$  and  $D(\text{CF}_3-\text{CF}_3) = 62$  kcal./mole. They point out that the relatively low value for  $D(\text{CF}_3-\text{CF}_3)$  is dif-



difficult to reconcile with the reported stability of this compound, and they suggest that the available value for  $\Delta H_f(C_2F_6)$  (88) might be in error.<sup>2</sup> The values derived by these two groups of workers have received further support from recent electron impact studies [see following section, and (55)]. In connection with the above value for  $D(CF_3-F)$ , it might be worth mentioning that the bond energy term in  $CF_4$  is calculated at  $\sim 116$  kcal./mole on the basis of the new values of  $-218.3$  kcal./mole for  $\Delta H_f(CF_4)$ , determined by Scott, Good & Waddington (144), and  $L(C) = 170$  kcal./g.atom and  $D(F_2) = 37.6$  kcal./mole. Luft (108) estimated a number of C—F, C—Cl and C—C bond dissociation energies in various organic fluorine compounds claiming the following values:  $D(CF_3-Cl) = 100$ ,  $D(CF_3-F) = 138$ , and  $D(CF_3-CF_3) = 107$  kcal./mole. These estimates do not agree with experimental values suggested by other workers (47, 55, 132, 134). Luft gives an extensive table of bond dissociation energies, which we consider rather speculative.

Page, Pritchard & Trotman-Dickenson (122) suggested that  $D(C-N)$  in azomethane could be identified with the activation energy for the decomposition of this compound determined at 46 kcal./mole by the toluene-carrier technique. However, more recent results (172) would indicate that this value is rather doubtful and that a higher value is more appropriate. Stewart & Cady (159) investigated the thermal decomposition of gaseous trifluoroacetylhypofluorite and believe that  $D(CF_3COO-F)$  is of the order of 25 kcal. However, in view of the complexity of the mechanism postulated for this reaction we feel that this value should be regarded as tentative. Schumacher and his students (43) extended their earlier studies of the properties of oxyhalogens and estimated the dissociation energy of the central Cl—O bond in  $Cl_2O_7$  at 48 kcal./mole. This value compares well with the Cl—O bond energy term of 50 kcal. calculated by them for this molecule. From the temperature coefficient of the homolytic dissociation of tetrafluoroenylhydrazine in different solvents, Chu & Weismann (38) calculated  $D(N-N)$  in this compound at 17 kcal./mole, which is by 14 kcal./mole lower than the  $D(N-N)$  value in tetraphenylhydrazine. This result is contrasted with the finding that  $D(C-C)$  in the comparable hexaaryl ethanes is almost constant irrespective of the nature of the aryl groups.

Gazith & Noyes (67) calculated  $D(\phi CH_2-I)$  at 37.4 kcal./mole from their kinetic data on the thermal and photochemical exchange reaction between benzyl iodide and iodine. This value agrees satisfactorily with the C—I bond strength in benzyl iodide derived by pyrolysis [39 kcal./mole (163)], from thermochemical data [36.5 kcal./mole (141)], or electron impact data [34.6 kcal./mole (106)]. However, it is lower than the recent thermochemical value of  $43.2 \pm 1.8$  kcal./mole given by Ubbelohde *et al.* (74). These workers estimated their value by measuring the heat of reaction  $\phi CH_2I + HI \rightarrow \phi CH_3$

<sup>2</sup> If the reaction  $CF_3 + C_2F_6$  is very slow, then the dissociation of  $C_2F_6$  into  $CF_3$  would be primarily followed by the dimerization of  $CF_3$  radicals, and  $C_2F_6$  would appear to be a stable compound.



+I<sub>3</sub>. Thus, they arrived at a value of  $34.3 \pm 1.2$  kcal./mole for the difference [ $D(\phi\text{CH}_2\text{—H}) - D(\phi\text{CH}_2\text{—I})$ ]. In their calculations, Ubbelohde *et al.* considered  $D(\phi\text{CH}_2\text{—H}) = 77.5$  kcal. If the latter dissociation energy is higher as discussed earlier, then the value given by Ubbelohde *et al.* for  $D(\phi\text{CH}_2\text{—I})$  would be even higher than 43.2 kcal. It seems that  $\sim 38$  kcal./mole is a more reliable estimate for  $D(\phi\text{CH}_2\text{—I})$ . By a similar method the following  $D(\text{C—I})$  values were calculated:  $D(\text{Me—I}) = 54.7 \pm 1.7$  (118),  $D(\text{Ph—I}) = 60.9 \pm 1.8$  (74),  $D(p\text{-MeO}\cdot\text{C}_6\text{H}_4\text{—I}) = 59.2 \pm 2$  (25), and  $D(\text{cyclo C}_6\text{H}_{11}\text{—I}) = 52 \pm 3$  kcal./mole (25). Other estimates for  $D(\text{Me—I})$ , are 54–55 (163),  $50.7 \pm 1.5$  or  $56.3 \pm 2.5$  (106), and  $\leq 53$  kcal./mole (20).

From a careful analysis of the kinetics of the thermal decomposition of chloroform, Semeluk & Bernstein (151) have deduced an upper limit of 72 kcal./mole for  $D(\text{CCl}_2\text{H—Cl})$ . From assumptions, the validity of which is questionable, Seubold (152) derived C—C bond dissociation energies for the series of cycloalkanes from C<sub>3</sub> to C<sub>8</sub>. These values were criticized by Pritchard & Trotman-Dickenson (129), who independently (130) proposed a somewhat less doubtful, but by no means more definite value of 74 kcal. for  $D(\text{C—C})$  in cyclobutane.

Takezaki & Takeuchi (169) investigated the decomposition of methanol induced by methoxy radicals produced by the pyrolysis of dimethyl peroxide. They derived an expression for the rate constant of the unimolecular decomposition of dimethyl peroxide ( $k = 4.1 \times 10^{15} \exp(-36,900/RT)$  sec.<sup>-1</sup>) and inferred that  $D(\text{CH}_3\text{O—OCH}_3)$  is  $\sim 37$  kcal./mole. This value is of the same order of magnitude as the O—O bond dissociation energies in other dialkyl peroxides listed in their paper. Bawn & Halford (11) extended their investigations of the rates of decomposition of initiators used in polymerization to include diacetyl and dilauroyl peroxides. The radicals produced in the primary dissociation process were removed by reaction with  $\alpha$ -diphenyl  $\beta$ -picryl hydrazyl as described previously (12). The unimolecular rate constants are found to be slightly dependent on the solvents. On the assumption that the activation energies may be identified with the O—O bond dissociation energies, they derived  $D(\text{CH}_3\cdot\text{COO—OOC}\cdot\text{CH}_3) \simeq 30$  kcal./mole and  $D(\text{lauroyl}\cdot\text{O—O}\cdot\text{lauroyl}) \simeq 30.4$  kcal./mole. Both of these values are in good agreement with the  $D(\text{O—O})$  values in acyl peroxides obtained by Szwarc *et al.* (139, 140). On similar grounds one may infer from the results of Bailey & Godin (6) that  $D(\text{O—O})$  in dibenzoyl and di- $\alpha$ -cumyl peroxides are  $\sim 29$  and 34 kcal./mole, respectively. Giguère & Liu (69) recalculated the thermodynamic functions for H<sub>2</sub>O<sub>2</sub> from recent spectroscopic and calorimetric data, and in conjunction with the value of 100.2 kcal. for  $D(\text{O—H})$  (52) estimated  $D(\text{HO—OH})$  and  $D(\text{DO—OD})$  to be  $\sim 51$  and 52 kcal./mole at 25°C. They tabulated the corresponding values for the temperature range 0 to 1500°K. These authors studied also the kinetics of the thermal decomposition of H<sub>2</sub>O<sub>2</sub> in a static system over the temperature range 300 to 600°C. (70). After correcting for the heterogeneous decomposition at the lower tem-

peratures, they derived the rate constant,  $k = 10^{13} \exp(-48,000/RT) \text{ sec}^{-1}$ , for the unimolecular reaction  $\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$ . They identified the activation energy with  $D(\text{HO}-\text{OH})$ . Furthermore, by using their recalculated values for  $\Delta H_f(\text{H}_2\text{O}_2)$  and the new value of 101.48 kcal. for  $D(\text{O}-\text{H})$  (8) they obtained  $D(\text{HO}-\text{OH}) = 48.5 \text{ kcal./mole}$ , which supports their kinetic results. Pritzkow & Müller (133) proposed a higher value of  $\sim 53 \text{ kcal./mole}$  for  $D(\text{RO}-\text{OH})$  in organic hydroperoxides. These authors used, however, in their calculations obsolete values for  $D(\text{HO}-\text{OH})$  and  $D(\text{O}-\text{H})$ .

In a recent article covering the literature up to 1954, Luft (109) reviews the experimental data leading to estimates for  $D(\text{RO}-\text{NO})$ ,  $D(\text{RO}-\text{NO}_2)$ , and  $D(\text{RO}-\text{OR})$ , and discusses the possible factors responsible for the relative instability of these compounds. He derives also the heats of formation of some alkoxy radicals and their energies of dissociation into smaller fragments. The same ground is covered by Gray in four recent papers (1, 75, 76, 77), containing references to more recent work and a complete set of tables of particular interest to workers in the field of oxidation of hydrocarbons. The thermal decomposition of nitrites and nitrates has been reinvestigated recently by a number of workers (97, 98, 124). Levy (97) concludes that  $D(\text{RO}-\text{NO}_2)$  in ethyl nitrate is  $41.2 \pm 0.5 \text{ kcal./mole}$ , a value slightly higher than the previously proposed, and that  $D(\text{RO}-\text{NO})$  in ethyl nitrite (98) must be smaller than the over-all activation energy for the decomposition which is 37.5 kcal./mole. From the recently determined heat of formation of nitromethane ( $\Delta H_f = -17.86 \text{ kcal./mole}$  at  $25^\circ\text{C}$ .) by Waddington and his colleagues (114) and the accepted values for  $\Delta H_f(\text{NO}_2)$  and  $\Delta H_f(\text{CH}_3)$  of 8 and 32 kcal./mole, respectively (180, 181), it follows that  $D(\text{CH}_3-\text{NO}_2) \simeq 58 \text{ kcal./mole}$ .

The mechanism of the thermal and photochemical decomposition of acetaldehyde has been disputed for many years. At present there is overwhelming evidence that the initial step in these reactions is the dissociation of the C—C bond. Letort (96), in a general review article covering his extensive work on the pyrolysis and oxidation of acetaldehyde, states that the activation energy for the process  $\text{CH}_3\text{CHO} \rightarrow \text{CH}_3 + \text{CHO}$  is  $78 \pm 6 \text{ kcal./mole}$  (119). This may be identified with  $D(\text{CH}_3-\text{CHO})$  and compared with Skinner's (141) value  $D(\text{CH}_3-\text{CHO}) = 71.5 \text{ kcal./mole}$  derived from thermochemical data. From a study of the photolysis of aldehydes, Dorman & Buchanan (49, 50) concluded that  $D(\text{H}-\text{CO})$  in formyl radical is  $\sim 23 \text{ kcal.}$ , a value based on the available thermochemical data and derived also from theoretical considerations of the potential energy surfaces for the reaction  $\text{HCO} = \text{H} + \text{CO}$ . In their thermochemical calculations they assumed  $D(\text{CH}_3-\text{CHO}) = 76 \text{ kcal./mole}$ . Klein & Schoen (91) have claimed that  $D(\text{H}-\text{CO}) \simeq 27 \text{ kcal./mole}$ . They found that illumination of formaldehyde with almost monochromatic light in the wavelength region of 3650 Å is effective in initiating the decomposition of  $\text{CH}_2\text{O}$ . This wavelength corresponds to  $\sim 78 \text{ kcal.}$  and may be considered as the upper limit for the first C—H bond dissociation energy in formaldehyde. Since  $D(\text{HCO}-\text{H})$  plus  $D(\text{H}-\text{CO})$  is  $\sim 105$

kcal./mole, it follows that 27 kcal. is lower limit for  $D(\text{H—CO})$ . The last two groups of workers point out that Calvert & Steacie (30) proposed 14 kcal./mole as a maximum value for  $D(\text{H—CO})$  from the interpretation of the kinetics of the photolysis of  $\text{CH}_2\text{O}$ , which, however, requires revision in view of the new evidence. Evidence for the high value of  $D(\text{H—CO})$  has been also adduced by Reed (136) from electron impact studies. His calculations lead to  $D(\text{HCO—H}) = 3.23 \pm 0.1$  ev and to  $D(\text{H—CO}) = 1.32 \pm 0.1$  ev ( $\sim 30.4$  kcal./mole). Further indirect evidence for the high value of  $D(\text{H—CO})$  may be obtained from the results of Szwarc & Taylor (168). These workers calculated  $D(\text{CH}_3\text{—CO})$  at 17 kcal./mole, and since the replacement of a hydrogen atom by a methyl group results generally in lowering the dissociation energy of the bond in question, one may arrive at a reasonable estimate of  $\sim 30$  kcal. for  $D(\text{H—CO})$ . Herzberg & Ramsay (81) established an upper limit of 37.7 kcal./mole for  $D(\text{H—CO})$  from the observed predissociation limits. Reed derived the additional values:  $D(\text{C}_6\text{H}_5\text{—CHO}) \leq 3.81 \pm 0.16$  ev (136),  $D(\text{CH}_3\text{—CHO}) = 2.82$  ev (137), and  $D(\text{C}_2\text{H}_5\text{—CHO}) = 2.90$  ev (137). Reed's value for  $D(\text{CH}_3\text{—CHO})$  of  $\sim 66$  kcal./mole is substantially lower than that given in Letort's paper.

At this juncture we feel it appropriate to point out that the derivation of bond dissociation energies from kinetic studies is based on the assumption that the activation energy of the process involving a bond rupture may be identified with the dissociation energy of the bond in question, i.e., with the endothermicity of the reaction. This assumption is valid only if the reverse process of recombination of radicals requires no activation energy. Over the last few years (158), evidence has been steadily accumulating to support the latter prerequisite, i.e., the collision efficiency for radicals such as  $\text{CH}_3$  (153),  $\text{CF}_3$  (4),  $\text{C}_2\text{H}_5$  (92), and  $\text{C}_3\text{H}_7$  (176) was found to be of the order of unity.

Moreover, the activation energy measures the slope of an Arrhenius line, i.e.,  $RT^2 \cdot \partial \ln k / \partial T$ , and this entity is not identical with the potential energy barrier which by definition is the bond dissociation energy. It appears that the difference between the former and latter energies is not more than  $\pm RT$  and therefore the kinetic method cannot give values for a bond dissociation energies better than  $\pm RT$ .

In applying the pyrolytic technique one has to ascertain that the molecule under investigation decomposes into radicals. This point is discussed by Szwarc (163). However, some molecules can decompose into more than two fragments by simultaneous rupture of more than one bond. Such cases were discussed recently by several workers. Carter, Chappell & Warhurst (32) drew attention to the peculiar features of the decomposition of organomercury compounds.<sup>3</sup> The sum of the two  $\text{Hg—C}$  dissociation energies,  $D_1 + D_2$ , is known from thermochemistry of these compounds. However, some compounds like  $\text{Hg}(\text{Me})_2$ ,  $\text{Hg}(\text{Et})_2$ ,  $\text{Hg} \cdot \text{Cl} \cdot \text{Ph}$ , and  $\text{Hg} \cdot \text{Br} \cdot \text{Ph}$  decompose

<sup>3</sup> This subject has been also discussed by Long (99).

with activation energy  $E < D_1 + D_2$ , and these reactions correspond to *normal* frequency factors of the order  $10^{13}$  to  $10^{14}$  sec.<sup>-1</sup> On the other hand, compounds like  $\text{Hg}(n\text{-Pr})_2$ ,  $\text{Hg}(\text{iso-Pr})_2$ , and  $\text{Hg}(\text{Ph})_2$  decompose with an activation energy  $E > D_1 + D_2$ , and the frequency factors of these decompositions are abnormally high, i.e.,  $\sim 10^{16}$  sec.<sup>-1</sup>. It is assumed, therefore, that the latter compounds decompose into three fragments simultaneously, i.e.,  $\text{Hg}$ , and two radicals  $\text{R}$ . The difference between these two types of decomposition is revealed by mapping the respective energy contours. It is shown that for a large  $D_2$ , the only feasible mode of decomposition is represented by the movement along the narrow potential energy valley leading to the hump  $E = D_1$ . This corresponds to a *normal* frequency factor. On the other hand, for small values  $D_2$  the decomposition is represented by a broad path (i.e., high frequency factor) leading to the broad plateau  $D_1 + D_2$ . In this case, the kinetic method does not yield information on the dissociation energy.

The same subject is discussed by Pritchard in two papers. His approach (128) is based on the treatment of the unimolecular reaction attributable to Polanyi and to Hinshelwood. The simple decomposition by rupture of one bond only requires accumulation of energy in one mode of motion; and then  $\epsilon^*$  (the critical energy), activation energy (the slope of Arrhenius line), and bond dissociation energy are all nearly identical. However, if the molecule can decompose by simultaneous rupture of two or more bonds, then  $k = \lambda \exp. (-\epsilon^*/kT) \cdot \Sigma(\epsilon^*/kT)^r/r!$ . In such a case  $\epsilon^* > D$  and activation energy is greater than  $\epsilon^*$ . The frequency factors of these reactions are very high. These ideas are developed further in a paper by Clark & Pritchard (42). They showed that the kinetics of the decomposition of various ketones can be accounted for on the hypothesis that  $\epsilon^* = D_1 + D_2$  and reasonable values for  $r$ . Thus, it appears that the activation energies obtained in the pyrolysis of diacetyl and benzyl methyl ketone should not be identified with the respective bond dissociation energies. This point was emphasized also by Szwarc & Taylor (168).

The more complex modes of decomposition seem to be plausible when the heat of dissociation of primary radicals is low. However, decompositions of acetyl, propionyl, and butyryl peroxides (139, 140) are interesting exceptions. It is shown by Jaffe, Prosen & Szwarc (86a) that the  $\text{R}\cdot\text{CO}_2$  radicals decompose exothermally, i.e., the *dissociation energies* of the  $\text{R}-\text{CO}_2$  bonds for  $\text{R}=\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , and  $\text{C}_3\text{H}_7$ , are negative; namely,  $-17$  kcal.,  $-14$  kcal., and  $-13$  kcal., respectively. Nevertheless, the activation energies and the frequency factors of these reactions are *normal*. It would appear that the activation energy of the dissociation process  $\text{R}\cdot\text{CO}_2 \rightarrow \text{R} + \text{CO}_2$  is high, and that the curve representing the stretching of the  $\text{R}-\text{CO}_2$  bond exhibits a pronounced hump.

#### ELECTRON IMPACT STUDIES

Within the last few years a considerable amount of data on bond dissociation energies has been obtained from electron impact studies. Some of these

data have already been referred to in previous sections. Field & Franklin (60) have written a comprehensive and critical review, dealing with the intricacies of mass spectrometric techniques and with the interpretation of the experimental results in light of modern theories of electron impact processes.<sup>4</sup>

The difficult problem of deciding whether excess kinetic energy or electronic energy, or both is associated with the fragment ions produced by the electron bombardment is discussed at great length. It is pointed out that the generally satisfactory consistency of the electron impact data implies that the positive ions (especially those formed from polyatomic molecules) are produced in the neighbourhood of their appearance potential with negligible kinetic energy. However, the kinetic energy of negative ions might be considerable. Obviously, the bond dissociation energies derived from electron impact data are subject to the uncertainty resulting from the undefined kinetic energy, which amounts probably to about 5 kcal./mole. Field & Franklin give an extensive compilation of values for bond dissociation energies. Many of the bond dissociation energies obtained by the electron impact technique compare favourably with the values derived by other methods. This may be considered as further evidence for the validity of the assumptions introduced in the interpretation of electron impact data and for the reliability of the method.

The ions produced in the initial fragmentation of the molecule on impact with an electron may break down further into smaller ions and radicals. Endothermicities of these reactions are a measure of the dissociation energies of bonds in the original ions. Field & Franklin (60) included also in their book an enlightening section on this subject, and attempted to interpret the mechanism of some organic ionic reactions in terms of the energies of the gaseous ions.

In a review article Craggs & McDowell (45) surveyed the field up to 1954, and discussed some of the theoretical implications of electron impact data. McDowell and colleagues (64, 115), using essentially monoenergetic electron beams, have been able to detect the formation of various molecular ions in all the excited electronic states expected on spectroscopic and theoretical grounds.

Lossing and colleagues have used mass spectrometers in conjunction with a special device permitting the formation of radicals by pyrolysis (104) or photolysis (58). From measurements of the ionization potential of radicals and their appearance potential from a number of compounds, numerous data on bond dissociation energies have been obtained. The earlier work of these workers on bond strengths in methyl, allyl and benzyl halides (106) has been recently followed up. Their values of  $31.6 \pm 2$  and  $33.2 \pm 2$  kcal./mole for  $D(C-I)$  in  $\beta$ - and  $\gamma$ -methyl substituted allyl iodides (116) compare reasonably well with  $D(\text{allyl-I})$  of 35.2 kcal./mole (106). The heats of

<sup>4</sup> The book has not been published yet. However, we had the opportunity to review their earlier manuscript covering the field up to December 1954.

formation of the allyl and of  $\beta$ - and  $\gamma$ -methyl substituted allyl radicals have been calculated and the corresponding  $D(\text{C—H})$  values are given:  $D(\text{allyl-H}) = 79 \pm 6$ ,  $D(\beta\text{-methylallyl-H}) = 76 \pm 3$ , and  $D(\gamma\text{-methylallyl-H}) = 80 \pm 3$  kcal./mole. Incidentally, their value for  $D(\text{C—H})$  in propylene is in excellent agreement with the value of  $76.5 \pm 2$  kcal./mole obtained by the toluene-carrier technique (148). Farmer & Lossing (56) have measured the ionization potentials of ethyl, isopropyl and propargyl radicals and derived  $D(\text{C}_2\text{H}_5\text{—H}) = 98.5 \pm 3$ ,  $D(s\text{-C}_3\text{H}_7\text{—H}) = 86.7 \pm 3.2$ ,  $D(s\text{-C}_3\text{H}_7\text{—I}) = 42.4 \pm 2.3$ ,  $D(s\text{-C}_3\text{H}_7\text{—Br}) = 58.8 \pm 2.3$ ,  $D(s\text{-C}_3\text{H}_7\text{—Cl}) = 73.3 \pm 2.3$ ,  $D(\text{CH}_2\text{C}\equiv\text{C}\cdot\text{CH}_2\text{—I}) = 45.7 \pm 3.2$  and  $D(\text{CH}_2\text{C}\equiv\text{C}\cdot\text{CH}_2\text{—Br}) = 57.9 \pm 3.2$  kcal./mole. At present, Lossing (105) believes these values for  $D(s\text{-C}_3\text{H}_7\text{—Hal})$  appear to be anomalously low and that they are to be considered as uncertain to more than  $\pm 5$  kcal./mole. These workers have also published (55) values for dissociation energies in trifluoro- and trichloro-methanes, such as  $D(\text{CF}_3\text{—H}) = 103 \pm 4$ ,  $D(\text{CF}_3\text{—F}) = 121 \pm 4$ ,  $D(\text{CF}_3\text{—Cl}) = 83 \pm 3$ ,  $D(\text{CCl}_3\text{—F}) = 102 \pm 7$ ,  $D(\text{CCl}_3\text{—Cl}) = 67.9 \pm 3$ ,  $D(\text{CCl}_3\text{—H}) = 88.9 \pm 3$ , and  $D(\text{CCl}_3\text{—Br}) = 49.5 \pm 3$  kcal./mole. The last two dissociation energies confirm earlier values obtained from kinetic studies and from toluene carrier technique (20a, 147). Their value for  $\Delta H_f(\text{CF}_3) = -117 \pm 2$ , is in excellent agreement with the estimates discussed earlier.

The behaviour of fluoromethanes on impact with electrons has been recently investigated by many other workers. One of the main difficulties has been to assign a correct value for the ionization potential of  $\text{CF}_3$  radical. Dibeler and co-workers (47) chose a value of  $9.3 \pm 0.2$  eV for  $I(\text{CF}_3)$  by combination of their data on appearance potentials for  $\text{CF}_3\text{Br}$  and  $\text{CF}_3\text{Cl}$  and the available values for  $D(\text{CF}_3\text{—Br})$  (147) and  $D(\text{CF}_3\text{—Cl})$  (134). They derived  $D(\text{CF}_3\text{—I}) \simeq 48.5$ ,  $D(\text{CF}_3\text{—F}) = 143 \pm 5$ , and  $D(\text{CF}_3\text{—CF}_3) = 115 \pm 2$  kcal./mole. Obviously the last two values diverge seriously from other estimates, discussed in the previous section. The assumptions involved in these calculations have been critically examined by Jacobson *et al.* (86), who point out that the discrepancy among the various values for  $I(\text{CF}_3)$  may be due to neglecting excess energy terms associated with the ion fragments.<sup>5</sup> Margrave (112) has shown that heats of reactions may be deduced from a proper choice of mass spectrometric appearance potentials. From an analysis of the data for methane derivatives, he derived  $\Delta H_f(\text{CH}_3\text{F}) = -59 \pm 2$  kcal./mole, provided  $D(\text{F}_2) = 36.6$  kcal./mole. These values, in conjunction with  $\Delta H_f(\text{CH}_3) = 32$  kcal./mole, lead to  $D(\text{CH}_3\text{—F}) \simeq 109$  kcal./mole. Foner & Hudson (61) have demonstrated the existence of  $\text{HO}_2$  radicals by mass-spectrometry and calculated the long sought values for  $D(\text{HO}_2\text{—H})$  and  $D(\text{H—O}_2)$  at  $89.5$  and  $47 \pm 2$  kcal./mole, respectively. They consider as fortuitous their agreement with the previous value of Robertson (142) for

<sup>5</sup> Recently Dibeler *et al.* (189) published mass spectrometric data for  $\text{C}_6\text{F}_6$  and suggested a tentative value of 145 kcal./mole for  $D(\text{C—F})$ .

$D(\text{H}-\text{O}_2)$  of  $46 \pm 9$  kcal./mole. More recently (62) these workers obtained  $D(\text{H}-\text{OH}) = 116 \pm 5$  and in conjunction with thermochemical data derived  $D(\text{O}-\text{H}) = 103 \pm 5$  kcal./mole. These values agree fairly well with estimates for these dissociation energies obtained by spectroscopic methods (7, 8, 52). Blanchard & LeGoff (18) have produced CS, SO, and  $\text{CCl}_2$  in electron impact experiments, and have suggested the following dissociation energies:  $D(\text{SC}-\text{S}) = 90 \pm 7$ ,  $D(\text{OS}-\text{O}) = 92 \pm 7$ , and  $D(\text{Cl}_2\text{C}-\text{Cl}) = 62 \pm 7$  kcal./mole.

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# ION-EXCHANGE RESINS AND MEMBRANES

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This review, which covers the period ending December 31, 1956, is concerned with those aspects of the field which are of interest to the physical chemist interested either in exchange resins or membranes per se or in their use as tools in the study of other physicochemical systems. Towards these ends, it was deemed necessary to include a survey of the preparative chemistry of these systems.

## PREPARATION OF RESINS

A good review of the preparative techniques for resins, particularly specific resins, covering the period up through 1954 was published [de Cat (1)]. The preparative procedures and properties of cation-exchangers prepared by the sulfonation of coal were summarized [Jurkiewicz, Zielinski & Laskowska (2)], while other articles dealt with the sulfonation of other natural products as cashew nut oils [Shah & Govindan (3)] and coals and asphalt [Goren (4)]. Carboxylic exchangers were prepared by heating coal at elevated temperatures in the presence of oxygen [Goedkoop (5)].

Phenolsulfonic acid-formaldehyde condensates were prepared where lignin was partially substituted for phenol, thus making the structure more porous with increased rates of exchange and no decrement in mechanical strength [Scipioni (6)]. Condensates with formaldehyde of naphthalenesulfonic acid [Bafna & Shah (7)], methylbenzenesulfonic acids and phenol [Kantebeen (8)], benzaldehydedisulfonic acid and phenoxycetic acid [Haagen (9)], were described, as well as ones using phenolsulfonic acid and prepared by azeotropic suspension condensation using different solvents [Ashida (10)]. Water could be removed at lower temperatures using the same techniques [Ashida (11)].

These condensation polymers do not find widespread commercial use, but these techniques still offer the most simple method of preparing certain experimental resins. Polymers of vinyl sulfonic acid, its salts and esters were reported [Park (12); Coover & Dickey (13); Stamicarbon (14)], while some of the properties of polyvinyl sulfonic acid were described [Kern, Herold & Scherhag (15)].

Since vinyl sulfonic acid polymers possess maximum charge density, a minimum of adsorptive sites and a strongly acidic exchange group, they appear to be the best systems for fundamental studies.

Improvements in procedures for sulfonated polystyrene were reported. The use of  $\text{SO}_3$  at low temperatures was described [Roth (16)], and it was reported that swelling of resins prior to sulfonation in liquid sulfur dioxide and other solvents led to improved properties [Bauman & Wheaton (17)]. Cross-linked polystyrenesulfonic acid resins were prepared by treating poly-

styrene beads with chlorosulfonic acid and paraformaldehyde [Stach (18)].

Potassium *p*-styrenesulfonate was homopolymerized and copolymerized with styrene and divinyl benzene (DVB) to form resins of variable polarity [Wiley & Reed (19)]. Sulfonamidostyrene was copolymerized with styrene and the product hydrolyzed to produce sulfonic resins of variable capacity [Wiley & Reed (20)]. The reactions produced some cross-linking, comparable to 0.2 to 1 per cent DVB. Terpolymers of *p*-sulfonamidostyrene, styrene and di-(*p*-vinylphenyl) sulfone produced sulfonic resins having swelling ratios from 1.3 to 22.3 and capacities varying from 1.5 to 5.5 meq./gm. [Wiley & Schmitt (21)]. In an interesting variation, poly-acrylamid was treated with formaldehyde and then sulfonated with sulfur dioxide, bisulfites and persulfates to produce a hydroxymethyl acrylamide sulfonic acid polymer [Suen & Schiller (22)].

As for carboxylic resins, polymethacrylic acid was cross-linked with PhCH:CHCH:CHPh [Sekino & Hirao (23)], while phenolphthalein condensed with formaldehyde gave a carboxylic cation resin of unusual properties [Bafna & Shah (24)]. Weak-base anion-exchange resins were prepared by cross-linking polyethyleneimine with ethylenedibromide [Shepherd & Kitchener (25)], while other resins were prepared from polyalkaleneamines, phenol and formaldehyde and from melamine, urea and formaldehyde [Kawabe, Sugimoto & Yanagita (26)]. These were compared with commercial resins prepared in the United States. Products of the cyanoethylation of aromatic amines were condensed with formaldehyde [Suda & Oda (27)], and strong-base resins prepared from trimethylamine, epichlorohydrin and formaldehyde were reported [Farbenfabriken Bayer (28)]. Anion-exchange resins were also prepared by addition polymerization. Chloromethylation of a copolymerize of styrene and ethylenedimethacrylate, followed by treatment with alkylamines yielded a quaternary ammonium resin [Arden (29)]. Resins were also prepared from divinyl pyridine or a copolymerize with vinyl quinoline followed by quaternization with an alkyl halide [D'Alelio (30)]. Pyridinium resins are not as useful as those containing the benzylammonium group because of the relative instability of the base form of the former. Cross-linked polyvinyl imidazole and quaternized polyvinyl imidazole resins were reported including ones prepared from the biquaternary compound of vinyl imidazole and  $\alpha^1, \alpha^4$ -dichlorodurene [Badische Anilin- & Soda-Fabrik Akt.-Ges. (31)], and N-vinyl carbazole polymers were described [Badische Anilin- & Soda-Fabrik Akt.-Ges. (32)]. These latter two resins possess unique metal-binding properties in their unquaternized form.

A series of resins having unique exchange groups or adsorbent properties were reported, usually employing techniques which are quite simple. Resins containing the esters of boric, arsonic and phosphoric acids were prepared by treatment of linear polyvinyl alcohol with the corresponding acids [Ashida (33)]. These polymers are cross-linked by di-esterification, and, while not as stable as the corresponding boronic, etc. compounds, can be used as anion-exchangers and, in the case of the borate esters, as specific resins for carbo-



hydrates and polyhydric alcohols. An arsonic acid cation-exchange resin was prepared by reducing nitrated cross-linked polystyrene, diazotizing the resin, then carrying out a Bart reaction [Parrish (34)]. This resin was a weak acid, capable of sorbing cations at pH values above 3, demonstrating no unusual selectivity.

A series of phenoxymethylphosphonic acids were condensed with formaldehyde to produce phosphonic acid resins [Walsh, Beck & Toy (35)]. Tertiary sulfonium anion-exchange resins were prepared from trianisylsulfonium chloride and formaldehyde [Directie van de Staatsmijnen in Limburg (36)]. Methods for the preparation of ammonium, sulfonium, phosphonium and arsonium compounds, ones which appear to be suitable for adoption to resin preparation, were described [Ripert, Baum & Thibaud Gibbs & Cie. (37)].

Sulfinic acid polymers were prepared from polystyrene or phenol-formaldehyde resins by treatment with carbon disulfide and dry hydrogen chloride in the presence of aluminum chloride, followed by treatment with sulfur dioxide, to form nuclear-substituted  $-SO_2H$  groups [Allen & Minsk (38)]. A series of new cellulosic ion-exchange materials was reported [Peterson & Sober (39)]. Finely divided cellulose was treated to produce acidic and basic substituents on the gel structure. Where the exchange capacity was held to 1 mmole/gm. or less, a stable and fairly nonswelling absorbent resulted; higher capacities led to gelatinous products which were unsuitable for separative procedures. Cellulose treated with 2-chlorotriethylamine became a weak base exchanger (DEAE), treatment with chloroacetic acid produced a carboxylic exchanger (CM), and treatment with  $POCl_3$  produced a phosphate (P) exchanger. Similarly, treatment of cellulose with triethanolamine and epichlorohydrin resulted in a quaternary ammonium exchanger (ECTEOLA). The exchangers were characterized by titration and by their protein absorptive capacity using equine CO hemoglobin and bovine plasma albumin. With the latter, the capacities varied from 30 to 120 per cent of the weight of exchanger. The exchangers were relatively stable to chemical attack, and proved to be particularly useful for separations of high molecular weight materials of biological origin.

It is often desirable to have non-conducting particles coated with exchange groups or particles of variable density. A technique for these systems was described where glass beads were treated with vinyl trichlorosilane; styrene and divinyl benzene were polymerized on the surface and then sulfonated [Berry & Caddell (40)].

The backbone of organic ion-exchange resins will ordinarily not withstand temperatures above  $120^\circ C.$  or strongly oxidizing conditions. The reported preparation of a number of perfluorosulfonic acids [Brice & Trott (41)] may lead to more stable matrices.

In recent years more attention has been paid to specific resins, ones which form complexes with certain ions or groups to the exclusion of others. Chelate resins were prepared by condensing phenolsulfonic acid and formalde-

hyde in the presence of 20 to 30 per cent citric or oxalic acid, to form resins which were altered in their general properties and which showed greatly increased absorption of Fe and Al [Lenskaya & Garanina (42)]. No details on the permanence with which these acids remained in the resin gel were given. Similar condensations in the presence of ethylenediaminetetraacetic acid, Trilon B and chromotropic acid were also reported [Klyachko (43)].

An iminodiacetic acid-type resin was prepared by the co-condensation of *m*-phenylenediaminetetraacetic acid with resorcinol and formaldehyde to give a resin having a capacity of about 0.5 meq./gm. [Blasius & Olbrich (44)]. These resins were used for analytical separations of transition metals from alkali metal and alkaline earth cations. Other polymeric analogs of iminodiacetic acid were reported, where alkaline polyamines were combined with chloracetic acid and chlorinated hydrocarbons [Monsanto Chemical Co. (45)]. An attempt was made to prepare an amino acid-type complexing resin by condensing *p*-hydroxyphenylglycine with formaldehyde [Ashida (46)], but a very low capacity resulted. Polymeric 8-quinolinal was prepared by coupling through diazotization to polyaminostyrene [Parrish (34)]. The resin formed chelates with a number of metals, but the reaction was very slow, probably due to the absence of a sufficient concentration of ionic groups.

Potassium-specific resins based upon dipicrylamine were prepared by known procedures [Skogseid (47)] with the nitration of polystyrene followed by its subsequent reduction, treatment with picryl chloride and final nitration [Woermann, Bonhoeffer & Helfferich (48)]. These were studied both in resin and membrane form. If rubber is sulfonated and then cured at 200°C. a resin is obtained which has a selectivity coefficient for K over Na of 5:1 [Nakazawa *et al.* (49)]; details were not given.

A specific resin containing the benzylthiol group was prepared from a chloromethylated cross-linked polystyrene using thiourea, followed by hydrolysis [Parrish (34)].

A mercarbide cation-exchange resin was prepared using the Hofmann synthesis to form the structure  $\text{ROCHg}_2\text{Hg}^+\text{X}^-$ , also written  $(\text{CHg}_2\text{O})_n^{n+}$  [Weiss & Weiss (50)]. The resin was insoluble in acidic, neutral and basic solutions, both aqueous and nonaqueous, and stable towards many oxidizing agents. It sorbed anions in the Hofmeister series; no data on selectivity coefficients were given. It would be of interest to compare its properties with those of the mercurated phenol-formaldehyde resins which are specific for mercaptans [Miles, Stadtman & Kielley (51)].

The resolution of racemic mixtures could be effected by a resin containing an optically active acid or base. Wool treated with sulfuric acid was capable of resolving small amounts of mandelic acid; similar resolutions could be effected by treating wool with sulfonic acid dyes [Bradley & Brindley (52)]. The sulfonic acids apparently neutralized the amino groups of the wool, and limited the number of resolving sites. A resin containing an optically active substituent was prepared by treating *N-p*-tolylsulfonyl-L-tyrosine with

phenol and formaldehyde [Bunnett (53)]. Information on its resolving power was not given. Poly-L-hydroxyproline having a D.P. of 40 was prepared; this polyampholyte was readily water-soluble and composed entirely of the L stereoisomer [Katchalski *et al.* (54)], making it a possible source of an active resin.

A few studies on the physical and chemical stability of resin systems were reported. Since ultrasonic waves are known to degrade polyelectrolytes [Saini & Ostacoli (55)], the degradation of ion-exchange resins by this technique is to be expected. The mechanical strength of sulfonated polystyrene cation-exchange resins was measured by ball-milling; mechanical strength decreased with increased water uptake by the gel [Sugihara & Izutani (56)].

The thermal decomposition of a quaternary ammonium anion-exchange resin in the chloride form was followed by titration [Leclerc & Samuel (57)]. The reduction of cation-exchange resins by hydrogen, ferrous, zinc and stannous ions, or by bisulfite was described [Directie van de Staatsmijnen in Limburg (58)]. The stability of a number of cation-exchange resins to permanganate, dichromate and bromate oxidizing solutions at varying pH levels was examined, with differences based upon the chemical nature of the matrix being observed [Lenskaya (59)]. Other studies showed that sulfonic resins based upon phenol and polystyrene could be oxidized with ferric chloride solutions, while methacrylic acid resins were stable under these circumstances [Losev & Tevlina (60)].

#### REDOX RESINS

New oxidation-reduction polymers were reported. Improvements in previously prepared materials were described; these usually involved introducing strongly ionized substituents into the otherwise hydrophobic structure so as to make for swelling and rapid exchange.

Copolymers of vinyl hydroquinone with 2,5-diacetoxystyrene and acrylic acid were reported [Minsk, Reynolds & Williams (61)]. A general method for the preparation of the *bis*-methoxymethyl ethers of vinyl hydroquinone, 3-vinyl catechol and 3-vinyl-*p,p'*-biphenol was described, as were procedures for preparation of polymers therefrom [Stern, English & Cassidy (62)].

Copolymers of vinyl hydroquinone and methylstyrene were sulfonated to produce water-soluble materials; copolymers with DVB were similarly treated [Ezrin & Cassidy (63)]. In subsequent work on the same system, virtually complete sulfonation of the nonhydroquinoid rings yielded a hydrophilic, strongly swelled and therefore highly permeable product [Luttinger & Cassidy (64)]. Oxidation with ceric ion proceeded well beyond that of the hydroquinone groups, but with bromine at low pH levels quantitative oxidation resulted (5.6 meq./gm.), while at high pH levels (pH 8.5) this oxidant also decomposed the resin. Oxidation or reduction was in all cases slow (half-times of 2 to 8 hr.) compared to ion-exchange (half-times being a few minutes), indicating that diffusion was not rate-determining in the former reactions.

Hydroquinone-formaldehyde condensates, prepared under both acidic and basic conditions, were examined for redox properties by oxidation with permanganate, ceric and ferric salts [Verplanck & Cassidy (65)]. Only the latter appeared to oxidize completely without degradation of the resin. These results agreed with earlier ones [Manecke (66)]; it appears that the relative success of Manecke's resins was attributable to their greater porosity.

Hydroquinone-pyrogallol condensates removed dissolved oxygen from a pH 7 phosphate buffer, the effluent oxygen concentrations being less than  $10^{-4}$  p.p.m. [Manecke (67)]. Also, a solution of hydroquinone and oxygen, when passed through a column of a hydroquinone-phenol-formaldehyde redox resin, produced an effluent containing hydrogen peroxide [Manecke (68)]. The function of the resin was to remove excess oxygen as well as inhibit the subsequent reaction with the quinone peroxide formed.

Metallic ions in exchange positions can be oxidized or reduced by non-eluting reagents. For example, Cu(II) and Fe(III) on a sulfonic acid cation-exchanger were reduced with iodide in acid solution; this procedure has analytical applications [Kakihana & Kato (69)].

#### EXCHANGE EQUILIBRIA

Since ion-exchange resin and membrane systems are concentrated solutions of polyelectrolytes constrained by cross-linking and therefore under high osmotic pressures, it is not at all surprising that progress has been slow in the direction of predicting their behavior from theoretical treatments of models or by thermodynamic or quasi-thermodynamic calculations. It is obvious that no quantitative theory of concentrated electrolytic or polyelectrolytic solutions will be forthcoming without a major theoretical breakthrough in the theory of liquids.

The use of quasi-thermodynamic treatments employing crude models has led to several predictions of qualitative validity. These have made good use of the Stokes-Robinson (70) treatment of electrolytic solutions. A few extensions of this treatment have appeared recently [Miller (71), Gleuckauf (72)]. Theoretical treatments of three different models have appeared. A parallel charged-plate model of an ion-exchange resin system was developed and its swelling properties at different external salt concentrations, mean activities of mobile electrolyte, electrical and osmotic pressures and wall potentials were calculated [Lazare, Sundheim & Gregor (73)]. The general methods of Verwey and Overbeek were employed, with the important exception that the normalization constant in the Boltzmann distribution expression was chosen so as to be self-consistent when the charging processes were carried out. It was shown that strong binding (low activity coefficients) would result, that the effect of the double layer was that of repulsion, countered by the elastic restoring force of the polymer matrix, and that modest wall potentials (60 mv.) could account for these effects. Specific binding phenomena were not considered.

The selective uptake of ions by a resin and its swelling characteristics were calculated for a cross-linked polyelectrolyte gel by postulating simple ion-pair formation between fixed sites and exchange ions [Rice & Harris (74), Harris & Rice (75)]. Swelling was calculated using the general methods of Flory and of Kuhn. This model demonstrated the general swelling properties of resin systems, and by suitable selection of parameters showed that selectivity would vary with resin composition. This treatment is a considerable advance over earlier work which limited itself to a rigid network [Gregor, Belle & Marcus (76)].

Taking as a model a quasi-lattice system where exchange ions form ion-pairs with fixed groups in doublet and triplet configurations, distribution coefficients were calculated by assuming a series of values in the two parameter equation developed; curves were fitted to the data for a number of uni-univalent exchange processes [Sakai, Seiyama & Ikari (77)].

The conditions of thermodynamic equilibrium in ion-exchange systems were summarized in an excellent manner and in some detail, with particular attention being paid to the choice of reference state [Holm (78)]. The various attempts to evaluate the pressure-volume free energy term were reviewed, as well as the difficulties in extrapolating from simple electrolytes to polyelectrolytes [Holm (79)]. Problems in the prediction of selectivity coefficients from isopiestic measurements on pure resins were summarized [Holm (80)].

The problem facing one who wishes to calculate selectivity coefficients from other data, particularly isopiestic data, are seen best by considering the same problem with a more simple system. Assume that the resin is a pure Donnan system consisting of an inner phase of a nondiffusible anion and mobile cations, in equilibrium across a membrane with a dilute electrolytic solution. Assuming that the concentration of immobilized groups in the resin could be varied at will, as by the imposition of an osmotic pressure, one could obtain solvent vapor pressures across the membrane for each of two exchange states and for intermediate mixed exchange states at Donnan concentrations varying from the infinitely dilute to concentrations as high as 10 molal, for example. It would be from these data that one could calculate selectivity coefficients for all mixed states at all total molalities, assuming that no diffusible electrolyte entered the inner phase from the outer solution phase. These calculations would be exact because all states intermediate between the reference state representing ideality and the final state could be reached by a reversible process on the same system. If selectivity coefficients were known for a system of relatively low concentration, isopiestic data above this concentration could be used for calculations in that range.

The system just described has not been treated. A resin of 8 per cent cross-linking does not necessarily possess the same entropy, for example, as a 2 per cent DVB system of the same molality; in fact, there is evidence that the thermodynamic properties of the two are different, and certainly quite different from those of the linear system [Gregor & Frederick (81)]. When

Gibbs-Duhem integrations are made across areas of experimental discontinuity, exact calculations are not possible. One could start with a DVB 2 resin and compress it through a series of compositions corresponding to those of the high DVB resins which do show strong effects; this is yet to be done.

The most extensive experimental test of the thermodynamic theory of ion-exchange processes [Gregor (82)] was provided by evaluating the pressure-volume term from isopiestic data, taking a 0.5 per cent DVB resin as a zero pressure standard, evaluating the ratio of cationic activity coefficients by the McKay (83) method, using the same resin system as a reference point [Myers & Boyd (84)]. Selectivity coefficients, calculated from an extensive array of isopiestic data, were found to agree with experimental values quite well with the alkali metals, and reasonably well with a few exceptions when the hydrogen ion was involved. The authors concluded that chemical heterogeneity in the highly cross-linked resins (large fraction of sulfonated DVB) was responsible for the large deviations observed there.

Differences between the activity coefficients for 2,5-dimethylbenzenesulfonic acid, 4,4'-bibenzylsulfonic and *m*-benzenedisulfonic acid (possible unit groups in high DVB resins) were cited as evidence for the nonconstancy of selectivity coefficients of sulfonated polystyrene resins [Bonner, Holland & Smith (85)]. Since association of the hydrophobic part of these acids plays a major role in determining their activity in water, the analogy on this basis is weak.

Thermodynamic properties of sulfonic cation-exchange resins of varying degrees of cross-linking and with different exchange cations were calculated from isopiestic data and from data on the distribution of diffusible electrolyte between resin and solution phases [Duncan (86)]. Similarly, selectivity coefficients were determined for all combinations of H, Li, Na, and K ions on polystyrenesulfonic acid resins of 5, 10, 15, and 25 per cent DVB content [Reichenberg & McCauley (87)]. With resins of lower cross-linking the ion giving the smaller swelled resin volume was almost always favored, but anomalies appeared with the 25 per cent DVB resin which was, unfortunately, not monofunctional. It was demonstrated that neglect of differences in resin phase activity coefficients for these cations, assuming that the pressure-volume term was entirely responsible for the distribution coefficients, did not in itself account for the data, but that it appeared likely that nonequivalent exchange sites were responsible. An excellent discussion of the difficulties in the exact prediction of  $K_d$  values was presented.

Cation-exchange equilibria were investigated with linear polystyrenesulfonic acid and linear copolymers of acrylic acid and methylmethacrylate by use of the equilibrium dialysis procedures where the polyelectrolyte concentration was about 0.05 molal. The results paralleled those for resins of low cross-linking in that the ammonium ion was preferred over sodium and lithium, while barium and calcium were strongly preferred [Hutschneker & Deuel (88)]. Lowered capacity made for lower selectivity, emphasizing the effect of chain charge.



The uptake of diffusible electrolyte from solutions of hydrochloric acid and sodium chloride by a sulfonic acid resin was measured in a series of dilute solutions [Baumann & Argersinger (89)], and was found not to affect the distribution coefficient. A theoretical justification was presented. In similar experiments with solutions of magnesium and calcium chloride [Ikari, Seiyama & Sakai (90)], it was observed that at concentrations above 0.1 molal the ratio of diffusible electrolyte in the membrane phase to that in the solution phase rose, but below this concentration the ratio also rose, an effect not generally observed in other resin systems. The formation of  $\text{MeX}^+$  ions may be responsible. A general statistical treatment was applied to the data.

Selectivity coefficients were determined for a number of exchange systems. The separation of  $\text{Na}^{22}$  from  $\text{Na}^{24}$  was achieved on a sulfonic acid resin column by elution with acid, with a calculated distribution coefficient of 1.0002 [Betts, Harris & Stevenson (91)]. Lower temperatures markedly favored the separation, suggesting that differences in hydration were responsible. Isotopic separations have now been reported for  $\text{Li}^6\text{-Li}^7$ ,  $\text{N}^{14}\text{-N}^{15}$ ,  $\text{K}^{39}\text{-K}^{41}$ , and  $\text{Ca}^{40}\text{-Ca}^{45}$ .

Selectivity coefficients and nonexchange electrolyte concentrations were determined for the chlorides of H, Li, and Na on a sulfonic exchanger from concentrated solutions [Kakihana, Maruichi & Yamasaki (92)]. Selectivity coefficients on polystyrenesulfonic acid resins of varying degrees of cross-linking were measured for ions which were generally preferred in the series  $\text{Ba} > \text{Ag} > \text{Sr} > \text{Ca} > \text{Cu}$  [Bonner & Livingston (93)]. The exchange capacity of a resorcinol-formaldehyde resin was measured [Gupta (94)].

The selective uptake of Na, Mg, and Ca by a phenolsulfonic acid resin was determined [Ikari, Seiyama & Sakai (95)]. The coefficients were fairly constant with composition; corrections for swelling were neglected and may account for the minor maxima observed. The behavior of a number of transition metals on the phenolsulfonic acid resin SF was examined [Meleshko (96)], as was magnesium-hydrogen exchange on a sulfonic resin [Yamabe (97)]. The uptake of calcium in the presence of sodium by a quebracho cation-exchange resin showed that this material was similar in this respect to phenolsulfonic exchangers [Virasoro (98)].

Titration curves for cross-linked polymethacrylic acid gels were shown to be essentially the same as those for simple polyelectrolytes [Gregor *et al.* (99)]. Carboxylic resins showed selectivities for alkali metals which were reverse those for sulfonic resins, probably the result of specific interactions between fixed and mobile groups, paralleling the behavior of the salts of acetic acid in this respect.

Polyacrylic and polymethacrylic acids were cross-linked with different agents and titrated in the presence of salt [Fisher & Kunin (100)]. The Henderson-Hasselbach expression was again obeyed, and the average ionization constant decreased linearly with the mole per cent of acrylate (presumably as defined by the composition of the monomer mixture) or with the degree of



swelling. Different cross-linking agents did not give identical curves; this may have resulted from different extents of participation in the polymerization processes. The swelled weights and volumes of another carboxylic resin neutralized with base at various ionic strength levels were reported [Kawabe & Yanagita (101)].

Titration curves for a bifunctional cation-exchange resin, prepared by the condensation of benzaldehydedisulfonic acid with phenoxyacetic acid and formaldehyde, were shown to reflect the particular properties of each exchange group [Cornaz & Deuel (102)]. The rate of exchange with ions which were strongly favored was found to be relatively rapid with this bifunctional resin, presumably due to its high degree of charge at all loadings. As regards anion-exchange, the uptake of a number of acids by a weak base polyethyleneimine resin was followed by potentiometric and swelling procedures. Acids served to neutralize the basic groups in the order of increasing molecular weight. The swelled weight of the resin decreased with increasing molecular weight of the acid, showing evidences of strong ion-pairing [Shepherd & Kitchener (25)]. The exchange of chromate with chloride, sulfate, and phosphate on weak and strong base anion-exchangers was examined at different pH levels [Didzar & Draganic (103)].

Empirical expressions are frequently applied to exchange equilibria; their applicability was evaluated [Hogfeldt (104)].

#### GENERAL PROPERTIES OF RESINS

Studies which do not fall into any particular category include one on the rates of swelling and deswelling of ion-exchange resin particles upon substitution of one ion for another as followed by direct observation; where swelled volumes are different, this method can be used to evaluate the attainment of equilibrium [Pulido (105)]. The heats of wetting of a number of resins in different ionic states were determined by direct calorimetric measurement [Matsuura (106)]. Heats of hydration for fixed and mobile ions are usually so large as to mask other thermal properties; as a consequence, they follow the usual hydration series.

Further work on the conductance of a packed column of sulfonic acid cation-exchange resin confirmed the work of Heymann and O'Donnell (107), and studies on mixed cationic resins showed no anomalies [Puri, Duke & Lomnes (108)]. The temperature coefficient for calcium ion conductance was approximately equal to that for sodium conductance. In an unusual study, the electrophoretic mobilities of phenolsulfonic acid-formaldehyde condensates were measured in aluminum, barium and sodium chloride solutions [Kramer & Freise (109)]. Resins of different molarities (0.3 and 1) migrated at nearly the same speed and the mobility fell off almost linearly with the logarithm of the salt concentration, reaching half of its limiting mobility ( $3 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1}$ ) in  $10^{-5} \text{ M Al}^{+++}$ ,  $10^{-4} \text{ M Ba}^{++}$  and  $10^{-3} \text{ M Na}^{+}$  solutions, in agreement with the degree of binding of these ions. Ac-

cordingly, the distribution of ions in the double layer appears to be a function of the Donnan potential, when corrected for specific ion-binding. Calculations of zeta potentials on these conducting systems necessarily required many approximations.

A number of studies were concerned with the adsorptive properties of exchange resins. Resins of fully sulfonated phenol or polystyrene still possess a high degree of adsorptive power. Fully neutralized carboxylic resins apparently show the lowest adsorptive power of the conventional resins, with adsorption rising sharply with degree of association. The sorptive properties of the porous form of sulfonated cross-linked polystyrene resins were described [Abrams (110)]; strong sorption by porous anion-exchange resins was also observed [Skold & Wilkes (111)]. Cation-exchange resins sorb basic dyes strongly, as do anion-exchange resins the acidic dyes [Grubhofer (112)]. Sorption appeared to be irreversible in that conversion of the dye to its non-ionized form reduced its solubility so as to make desorption difficult. Sorbed indicator dyes indicated the pH of the resin phase [Steuerle (113)], particularly in fairly concentrated (0.1 to 0.5 *M*) buffers [Nagase & Kawai (114); Leclerc & Samuel (115)]. High molecular weight exchange ions can be sorbed so strongly that capacity to large ions is reduced, with smaller ions not affected [Krzysztofowicz & Woycicki (116)]; evidence for the non-exchange adsorption was presented [Davydov & Skoblionok (117)].

The adsorption of nonelectrolytes by resins was reviewed [Samuelson (118)]. This effect is often quite strong, and it has found several applications. The adsorptive properties of a number of anion-exchange resins of different basicities and porosities were compared [Iwashina, Miyao & Asami (119)]. Adsorption of urea from blood by a carboxylic resin was demonstrated [Bonanome & Begani (120)]. While urea is not sorbed appreciably from aqueous media by cation-exchange resins, sorption from methanol solutions is strong, particularly with aryl-substituted ureas so that separations are possible [Grubhofer & Schleith (121)].

Since the distribution of acetic and butyric acids between aqueous and sulfonic resin phases is somewhat different, partition chromatography using water as eluant produces a separation [Reichenberg (122)]. Sorption of other organic acids and of alcohols was also studied [Reichenberg & Wall (123), Bafna & Govindan (124)], as was that of phenols by anion-exchange resins [Chasanov, Kunin & McGarvey (125)].

Nonelectrolytes such as alcohols and glycols which can be salted out of aqueous solutions can be separated on ion-exchange resin columns because their solubility in the resin phase is relatively unaffected by the presence of salt [Sargent & Rieman (126)]. The distribution of ethylene glycol and glycerol in the presence of salt in a sulfonic acid resin system was further evaluated [Simpson & Bauman (127), Asher & Simpson (128)].

A strong base anion-exchange resin sorbed iodide selectively from mixtures with chloride, the iodide could be oxidized *in situ* and adsorbed as such,

following which further exchange took place [Sekino (129)]. The sorption of iodine was strongest by resins in the most ion-paired state, i.e., the reverse of the lyotropic series.

Since exchange resins can differentiate between anionic and cationic species, they have been used to study complex ion formation. The reaction between a number of glycols and boric acid to form borato-complexes was studied on an anion-exchange resin column in the borate form [Sargent & Rieman (130)]. Distribution coefficients and formation constants for the complex were calculated. Cationic and anionic phosphato-complexes of a number of metals were similarly studied [Holroyd & Salmon (131)], as were those of metallic cations with other complexing agents [Chambionnat & Miede (132); Ishimori & Okuno (133); Neuman *et al.* (134)].

Linear or cross-linked polyelectrolytes form metal chelate complexes of high orders of stability [Gregor (135)]. Complex ions formed in an ion-exchange resin were studied by direct spectrophotometric measurement [Fujimoto (136)], and by infrared studies of carboxymethylcellulose films neutralized with Na, K,  $\text{NH}_4$ , Ca, and Sr ions at different pH levels [Sobue & Tabata (137)].

The uptake of copper and zinc by hydrogen-form sulfonic resins and carboxylic resins was measured by direct analysis [Cornaz & Deuel (138)]. With the carboxylic resins,  $\text{Cu(II)}$  was favored over  $\text{Cu(NH}_3)_2\text{(II)}$ , due to competitive complex formation. An anthranilic acid condensate was studied employing selectivity coefficient, conductance, titration and swelling measurements. All methods gave consistent results, showing that strong complexes were formed with Co, Ni, and Zn, weaker ones with Ca and Ba, while Li and K gave little evidence for complex formation [Jenckel & Lillin (139)].

#### KINETICS AND COLUMN OPERATION

The kinetics of ion-exchange processes was reviewed [Helfferich (140), Becker-Boost (141)]. The self-diffusion of sodium from a bath into a rod of cation-exchange resin was studied [Richman & Thomas (142)]. This arrangement made for a minimal thickness of the unstirred film, such that even in 0.01 *N* solution particle diffusion was rate-determining. The role of non-exchange electrolyte in increasing the mobility of exchange cations and decreasing the temperature coefficient was amplified. Self-diffusion of sodium and its exchange with hydrogen were measured [Mamontova (143)], as was Na-K exchange [Sujata, Banchero & White (144)]; the rate of exchange of alkali metal cations for hydrogen was measured in a stirred-bath system employing dilute solutions so that film diffusion was rate-determining, with a film thickness of 3  $\mu$  [Dickel & von Nieciecki (145)]. Rates of self-diffusion of Rb in a sulfonic and in a fully neutralized carboxylic resin were found to be of the same order [Nair, Govindan & Bafna (146)], showing that the porosity of the resin determines, to a large extent, the rate of exchange reactions.

The enormous resolving power of ion-exchange chromatography was

demonstrated when it was shown that the presence of  $C^{14}$  in the 1- or 2-position in an  $\alpha$ -amino acid gave it a different selectivity coefficient [Piez & Eagle (147)].

The composition of the eluate resulting from citrate elution of rare earths was found to conform closely with values calculated from distribution coefficients, employing only material balance considerations because steady-state conditions were being evaluated [Spedding & Powell (148)]. A theory was derived for the conditions of ion-exchange chromatography where the eluant was both discontinuously and continuously graded [Freiling (149)]. A simplified expression was found to give peak location and shape. The use of empirical equations for ion-exchange kinetics was evaluated, and it was shown that under most circumstances the approach to equilibrium in chromatography is so close that simplified expressions can be used [Glueckauf (150)].

A mathematical theory of column kinetics was derived, and tested using Na, K and Rb exchange [Todes & Rachinskii (151)]. Subsequent theoretical and experimental studies were also carried out [Todes & Rachinskii (152), Rachinskii & Todes (153)]. The theory of the column separation of cations by elution with complexing acids was examined in detail, and applied to the separation of Co(II) and Fe(II) on a cation-exchange resin [Elovich & Motorina (154)].

Another theoretical study of ion-exchange chromatography was applied to systems showing nonlinear equilibria and where film or particle diffusion was rate-determining [Hiester *et al.* (155)]. The spreading of chromatographic bands was evaluated by self-diffusion experiments, and it was shown that diffusion could not account for the spreading, but rather it seemed to be due to nonuniform flow [Dzhagatspanyan & Tunitskii (156)]. Further calculations on the effect of diffusion in ion-exchange chromatography were made [Bastian & Lapidus (157)]; concentration profiles in columns were calculated [Byrne & Lapidus (158)].

#### NONAQUEOUS EXCHANGE AND CATALYSIS

More attention is being accorded the use of nonaqueous or mixed solvents. The swelling of resins in acetone-water mixtures and the distribution of these solvents was measured [Davies & Owen (159)].

The distribution coefficient for the ammonium-hydrogen pair with a sulfonic acid resin was about the same in methanol as in water, while sodium was preferred over hydrogen in methanol as compared to water [Gable & Strobel (160)]. The preference for silver over sodium in methanol was 3 to 5 times that in water. Separations of the alkali metals were improved in acetone-water mixtures [Davies & Owen (159)], as were separations of aliphatic and aromatic carboxylic acids in dioxane-water mixtures [Davies & Owen (161)].

The rate of sorption of butylamine by a sulfonic acid resin in ethanol-water mixtures was measured [Wilson & Lapidus (162)]. The rate was con-

trolled by particle diffusion and dropped off sharply as the weight fraction of ethanol rose to 0.9.

Cobalt and nickel were separated on an anion-exchange resin in a molten urea medium [Sansoni (163)]. The use of the more unusual solvents remains largely unexplored.

While catalysis by means of ion-exchangers offers many interesting possibilities, progress in this field has been slow, probably the result of a lack of resins tailored for the purpose. Recent advances in catalysis were reviewed [Glenat (164); Lister (165)].

The rate of alkaline hydrolysis of esters in alcoholic media by quaternary ammonium resins in the hydroxide state was found to be second-order [Samelson & Hammett (166)]. Rates were lower with a benzyltrimethylammonium resin than with ethyl-, hexyl- or benzyl-substituted resins, particularly with larger esters, although the rate was not diffusion controlled.

The following catalysis studies were reported: aldol- and ketolcondensations by anion-exchange resins [Pallaud & Austerweil (167)]; cyanoethylation reactions of organic amines by carboxylic resins [Suda & Oda (27)]; hydrolysis of sucrose with sulfonic acid resins [Fodor & Hajos (168)]; formation of methyl glycosides and propylidene derivatives by a sulfonic acid resin [Erne (169)]; esterification of citric acid and phthalic anhydride by butanol by a sulfonic acid resin [Ruzicka & Medonos (170)]; paraldehyde to acetaldehyde and the base catalysis of the latter to acetaldol and crotonaldehyde using mixed resins [Mastagli (171)].

In another kind of study, anion- and cation-exchange resins were treated with soluble Pd salts, and the metal precipitated in the resin void used as a catalyst for the hydrogenation of maleic acid [Mariani & Spinelli (172)]. Catalytic activity varied with preparative procedures.

#### MEMBRANES

Ion-selective membranes are essentially films of polyelectrolytes or of ion-exchange resins. All of the fundamental properties of ion-exchange resins are exhibited by the membranes, and several additional properties, particularly those pertaining to irreversible processes, become available for study. Fundamental investigations are now being centered, as a consequence, upon membranes rather than on resins, and the information gathered helps in turn to elucidate resin behavior.

An extensive review of transport processes across natural and synthetic membrane systems was presented, with particular attention given to model studies which produce effects similar to those found in biological systems [Teorell (173)]. A brief review of the application of quasi-thermodynamics and of the thermodynamics of irreversible processes to various membrane models was presented [Scatchard (174)].

Many theories of the behavior of ion-selective membranes have appeared in recent years. A few additional studies are of interest. The McMillan-Mayer method was used to treat a Donnan membrane system [Hill (175),

176)). The general phenomenological equations of nonequilibrium thermodynamics were applied to dissipative processes occurring in an ion-selective membrane system, following the Staverman (177) treatment [Sakai & Seiyama (178)]. The influence of convection in the transport of ions and of solvent across ion-selective membranes was calculated, with comparisons drawn to the method of Kirkwood (179) [Schlogl (180)]. An expression for the potential of a membrane separating two solutions of different temperature was derived [Hills, Jacobs & Lakshminarayanaiah (181)].

A number of preparative techniques were reported. Homogeneous ion-selective membranes were prepared by dissolving a polyelectrolyte and a film-forming water-insoluble polymer in a common solvent, casting a film therefrom which upon drying produced membranes of low ohmic resistance and high selectivity [Gregor & Wetstone (182)]. Cation-exchange membranes were prepared from phenolsulfonic acid, polyvinyl alcohol, and formaldehyde [Ikari, Seiyama & Sakai (90)], and membranes were cast from solutions of viscose and sodium carboxymethylcellulose, then hardened by boiling in salt solutions [Lorimer, Boterenbrood & Hermans (183)].

A phenosulfonic acid-formaldehyde condensate was made in plate form by stopping the cure before all of the solvent present had evaporated, obtaining a resin of low (1.5 to 1.9 meq./gm.) capacity [Brun (184)]. Mechanically strong membranes were made by carrying out the condensation in a fritted glass disc. Highly selective anion-permeable membranes of low resistance were prepared by the polymerization of ethyleneimine and epichlorohydrin [Nishihara, Mineki & Sekino (185)]. Anion-exchange membranes were prepared by the condensation of phenol, an alkylene polyamine and formaldehyde in the presence of water [Juda & Kasper (186)], and additional patents describe several different preparative procedures [Clarke (187)].

Protein membranes prepared from precipitated films of actomyosin showed reasonably high concentration potentials which decayed with time and which were pH sensitive [Richter & Bonhoeffer (188)]. Natural polyelectrolyte gels including collagen and alginates were prepared in plate form and their exchange, swelling and optical properties examined [Thiele & Andersen (189)].

Data for the conductance and swelling of a cross-linked polymethacrylic acid gel neutralized with potassium hydroxide [Despic & Hills (190)] were compared with an expression derived for the relative conductance of a uniform gel with all pores larger than the diffusible ions [Mackie & Meares (191)]; good agreement was obtained for gels having a polymer volume fraction of 0.2 to 0.5 [Meares (192)]. The uptake of nonexchange electrolyte by sulfonic acid membranes was measured for a variety of salts [Krishnaswamy (193)]. This uptake increased with cationic valence and atomic weight.

A number of studies which combined several techniques were reported. The conductance, transference and potentiometric properties of a carboxylic membrane were measured, and fair agreement was found between measured

concentration potentials and those calculated from transference experiments [Lorimer, Boterenbrood & Hermans (183)]. Similarly, transference measurements made across sulfonic and carboxylic membranes with a number of univalent ions were coupled with selectivity coefficient measurements to calculate bi-ionic potentials [Bergsma & Staverman (194)]. Agreement with measured bi-ionic potentials was generally quite good. With more porous films low potentials apparently resulted from water transport.

In other, similar experiments, the rate of diffusion of salt and water across a heterogeneous anion-exchange membrane separating ammonium chloride solutions of different concentrations was measured, transference experiments gave electrical transport numbers and electro-osmotic transport values, and these combined with potential measurements were found to agree reasonably with theoretical predictions [Ishibashi, Seiyama & Sakai (195)]. The discrepancy between transport numbers calculated from potential equations and ones determined by Hittorf measurements was also found to be due to water transport [Oda *et al.* (196)].

The transport number of a permeable species was found to decrease with increasing current at high current densities in the absence of stirring due to the resultant concentration overvoltage [Kressman & Tye (197)].

The electro-osmotic transport of water through a sulfonic membrane was determined largely by its water content [Oda & Yawataya (198)]; further studies on the transport of water accompanying electrodialysis across a sulfonic membrane were reported [Nagamatsu, Seiyama & Sakai (199)]. The amount of water transported across heterogeneous cation-permeable membranes along with cations was found to follow the Hofmeister series with the alkali and alkaline earth metals, while with quaternary ammonium cations abnormally large amounts were transported [Winger, Ferguson & Kunin (200)]. This latter effect was probably due to swelling of the resin in the membrane. Electro-osmotic data were used to calculate hydration numbers of alkali metal cations [Despic & Hills (201)]; calculations of this type necessarily require crude approximations.

The simultaneous diffusion of electrolytes and nonelectrolytes across sulfonic membranes was investigated [Manecke & Heller (202)]. With nonelectrolytes the rate of permeation was found to depend upon their partition in the resin phase and upon the exchange cation present. The sorption of ethanol and its rate of permeation across a sulfonic acid membrane was also studied, and it was observed that the substantial fraction of the alcohol bound by the resin (as calculated from its distribution) was not diffusible [Mackie & Meares (203)].

The rate of exchange of hydrogen for sodium and calcium across a sulfonic acid membrane was measured at different rates of stirring, as was the rate of anion-exchange [Stewart & Graydon (204)]. Interdiffusion rates for cations were calculated. The diffusion of water and magnesium through a sulfonic membrane in the magnesium and sodium states was measured [Nagamatsu, Seiyama & Sakai (205)].



Concentration potentials for potassium and magnesium chloride solutions across a phenolsulfonic acid-formaldehyde membrane were measured at different rates of flow [Brun (184)]. Concentration potentials fell off almost linearly with the square root of the mean concentration, the effect being quite strong with magnesium chloride due to the relatively strong binding of this ion. Potentials were also found to be in inverse variation with the square root of flow rate. Potential differences between sodium chloride, sulfate and polyvinyl sulfate salts measured across a sulfonic membrane were found to be lower than those calculated from the Nernst equation [Nagasawa & Kagawa (206)]. These deviations were believed due to abnormally low activity coefficients of mobile ions in the membrane.

The theory of bi-ionic potentials was surveyed [Dray & Sollner (207)], and their measurement showed that the permeable ions followed the Hofmeister series, that the nature of the nonpermeable ion was of little consequence, and that a reduction in porosity generally made for higher potentials [Dray & Sollner (208)]. Bi-ionic potentials were also measured with the same two diffusible ions being present on each side of the membrane [Dray & Sollner (209)]. Experimental potentials agreed fairly well with those calculated from simple bi-ionic systems. This work was continued with 4-ion systems, again with reasonably good agreement with theory [Dray & Sollner (210)]. It is evident that the integral mobility of an ion in these membrane systems was not affected by other ions present. This may be a property of the nonswelling membranes used because diffusion coefficients in resin systems are affected by the presence of other ions which make for increased swelling. In a subsequent report, the rate of exchange of ions across ion-selective membranes was correlated with their bi-ionic potentials [Neihof & Sollner (211)]. Other studies on bi-ionic potentials measured with univalent cations across a sulfonic acid membrane were reported [Brun & Engan (212)]. When a membrane system was stirred by a jet of solution normal to the surface, large changes in potential were observed, particularly with exchange ions of different valence [Scatchard & Helfferich (213)]. The composition of the membrane adjacent to each solution was calculated from these potential measurements, and demonstrated the strong selectivity for polyvalent ions. The Nernst-Planck treatment of a membrane system and its adjacent unstirred layers led to calculated concentration profiles [Helfferich (214)]. Stirring parallel to the membrane face led to particularly thin unstirred films and a minimization of concentration overvoltages [Gregor & Wetstone (182)].

The specific uptake of calcium as opposed to potassium occurred with certain sulfonic and carboxylic membranes without concomitant immobilization of the former ion; this led to large membrane transport numbers for Ca [Gregor & Wetstone (182)]. Specific transport tended to disappear at high current intensity, probably as a result of dissociation of the complex by the high field strength present.

Another specific-type membrane was prepared from a dipicrylamine

resin [Woermann, Bonhoeffer & Helfferich (48)]. The selectivity coefficient for K over Na varied almost linearly from unity at DVB 1 to a maximum of 2.3 at DVB 23, falling at higher DVB levels. Resin volumes were greatest for Li, decreasing steadily with increasing molecular weight to Cs, the value for H being even lower. Rate experiments gave diffusion coefficients for Na which were about 20 per cent higher than for K, probably a reflection of the lower degree of swelling. When the resin was made in membrane form, the measured bi-ionic potential for Na vs. K agreed with that calculated from selectivity and rate data, the potential being,  $E = 0.059 \log K_{Na}^K (D_K / D_{Na})$ .

A number of other studies of interest were reported. If a mosaic of cation-permeable and anion-permeable membranes separates a solution of two different concentrations, the ionic current can be calculated from the resistance of the circuit and the differences in the potential of each solution. An experimental model was set up and the theoretical calculations verified [Neihof & Sollner (215)].

The junction potential between two plugs of sulfonic resin particle, each equilibrated with a sodium chloride solution of different concentration, was found to conform to that calculated for an equivalent parallel-series circuit [Spiegler, Yoest & Wyllie (216)]. In another study, current was passed across a pair of cation-permeable and anion-permeable membranes cemented together; polarization ensued rapidly and current was carried by products of the ionization of water [Frilette (217)]. Electrodialysis with ion-selective membranes was employed to concentrate sodium chloride solutions from 0.01 to 1 M [Kuwabara, Seiyama & Sakai (218)].

A series of papers on precipitation membranes, first described by A. C. Becquerel in the period 1867 to 77, have appeared recently. These membranes are formed by precipitating an insoluble salt in the pores of a diaphragm, with the precipitate being copper ferrocyanide [Bonhoeffer *et al.* (219)], barium sulfate [Hirsch-Ayalon (220)] or copper bicarbonate [Straub (221)]. Some of these membranes are permeable only to certain species of anions or cations, and they often produce high potentials which are combinations of diffusion potentials and electrochemical potentials. The permeability of Co, Ni and Ag ferricyanide membranes to inorganic salts and to sucrose was measured [Hasan, Malik & Bhattacharya (222)].

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